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Factors Affecting Trace Metal Mobility in Subsoils.

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Louisiana State University and Agricultural & Mechanical College

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Kotuby-Amacher, Janice, Ph.D.

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FACTORS AFFECTING TRACE METAL
MOBILITY IN SUBSOILS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Marine Sciences

by
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ABSTRACT

The transport of metals to groundwater below hazardous waste sites is of great environmental concern. The movement of a particular metal is determined by (1) the soil's chemical and physical properties, (2) the amount and form of the metal, and (3) the composition of the soil or waste solution with which the metal is associated. Field and laboratory studies were conducted to examine these factors affecting metal mobility in subsoils. The objectives of the field studies were to determine the distribution and chemical forms of metal contaminants in subsoil at sites with known or suspected potential for groundwater contamination. The objectives of the laboratory studies were to determine the effect of soil properties, solute concentration, solution composition, and redox status on the retention and transport of Cd and Pb in subsoil materials.

In the field and laboratory studies, the soil properties controlling Pb retention and mobility were pH, CEC, metal oxides (Mn oxides, amorphous Fe oxides, and free Fe oxides), and soil particle-size distribution. Retention of Cd was controlled by pH, CEC, amorphous Fe oxides, and particle-size distribution. Copper mobility was controlled by the three metal oxides. The Fe oxides (amorphous and crystalline) controlled Ni and Zn retention. Arsenic retention was controlled by pH, CEC, and the metal

oxides. Redox potential was also important in Cd and Pb retention, with greater metal retention under oxidizing conditions.

In the laboratory studies, higher concentrations of Cd and Pb resulted in lower proportions of metals being retained by the soil. Therefore, the greater the concentration of the metal, the faster it will move through the soil. The retention of Pb was greater than Cd. The retention of Cd and Pb was greater in a dilute salt solution (0.005M $\text{Ca}(\text{NO}_3)_2$) and in a simulated oil field waste. Retention was less in a synthetic municipal landfill leachate and simulated acidic metals waste. Organic complexation of Cd and Pb reduced their retention and thus increased their mobility. The low pH of the acidic metals waste and competition from other metals reduced Cd and Pb retention in this waste. It was concluded that the composition of the waste solution may override soil factors in controlling trace metal mobility.

CHAPTER 1

INTRODUCTION

BACKGROUND

The transport of metals to groundwater below hazardous waste sites is of great environmental concern. The movement of a particular metal is determined by the amount and form of the metal, the soil's chemical and physical properties, and the composition of the soil or waste solution with which the metal is associated. The soil properties affecting metal retention/release and transport include bulk density, surface area, particle-size distribution, pH, redox status, ion exchange capacity, amount of organic matter, type and amount of metal oxides, and type and amount of clay minerals (Amacher et al., 1986). Soils with a wide range of these properties were selected for this study except that all of the subsoils materials had typically low levels of organic matter. Soil organic matter, at levels commonly found in surface soils and sediments, is one of the primary immobilizing processes for trace and toxic metals (Gerritse and van Driel, 1984; Levi-Minzi et al., 1976). Subsoils, usually beginning 15 cm to 30 cm beneath the surface, generally contain so little naturally-occurring organic matter that it becomes important to focus on other metal retention processes in the region between surface soils and groundwater.

In a hazardous waste dump or landfill, a variety of types of waste may be present that may become mixed with metals at or beneath the site. Mixtures of metals and other wastes may interact to influence the mobilization/immobilization of metals. The presence of toxic metals with acidic wastes, for example, would greatly enhance the leaching of metals beneath the initial disposal zone toward groundwater. This is a set of parameters that has not been thoroughly addressed in the toxic metals studies associated with sludge-amended soils or dredged materials as very acidic conditions are rarely encountered in these situations. Also, certain organic wastes in high concentration may affect the mobility of metals. It is likely there are many locations where waste mixtures are present that may enhance or have already enhanced the leaching of metals to groundwater. The concept of facilitated transport of metals in waste mixtures has not yet received the research attention it deserves. This research was designed to begin to examine this topic.

LITERATURE REVIEW

The migration of trace elements through soils depends upon the properties of the leaching solution, the soil, and the trace element. The physical properties of the leaching solution (i.e., specific weight, viscosity, surface tension) determine the mobility of the individual components and their miscibility (Jackson, 1980). The chemical properties of the leaching solution (i.e., pH, total organic carbon, chemical oxygen demand, carbon dioxide tension, soluble inorganic salts, total soluble Fe content, specific polluting element concentration, age of leachate, and

amount and strength of organic chelates and inorganic complex ion formers present) also affect the mobility of trace elements.

The trace metals must be in the soluble phase or associated with mobile particulates to be transported through soil. Therefore, various soil factors, such as bulk density, surface area, particle-size distribution, pH, redox status, ion exchange capacity, amount of organic matter, type and amount of metal oxides, and type and amount of clay minerals, affect metal migration through soil (Amacher et al., 1986).

For example, Korte et al. (1976) and Fuller (1978) found that the movement of lead (Pb) was related to soil texture with Pb migrating deeper in the soil column for those soils coarser in texture. Cadmium (Cd) retention capacity increased as the percent clay increased (Page et al., 1981). The cation exchange capacity (CEC) also plays an important role in trace metal retention by soils. Miller et al. (1976) concluded that CEC was the primary soil factor controlling Cd retention capacity.

Soil pH is probably the most important factor controlling metal retention by soils. Lead solubility has been found to decrease as pH increased (Santillan-Medrano and Jurinak, 1975). Lead retention increased with increasing pH because of the increase in PbOH^+ activity at the expense of Pb^{2+} , the latter ion having a higher solvation energy barrier to adsorption. (Brown, 1979). The retention of Pb by hydrous ferric oxides is favored at higher pH values (Gadde and Laitinen, 1974). Lead retention by hydrous ferric oxide increased steadily with increasing pH (Gadde and Laitinen, 1973). The retention of Pb by hydrous Mn oxide increased linearly in the pH range pH 2 to pH 6 (Gadde and Laitinen, 1974). Cadmium retention also increased with increasing pH (Cavallaro and McBride, 1980; Elliott, 1983; Kuo and Baker, 1980).

Griffin and Shimp (1978) reported that, in general, retention of As(III) on clays increased as pH increased in the range pH 3 to pH 9, while for As(V), maximum retention occurred around pH 5 (Gulens et al., 1979). Page and Pratt (1975) proposed that in acid soils, dissolved As probably reacted to form insoluble Fe and Al arsenates, while in calcareous soils, As solubility was limited by the formation of Ca arsenate.

The mineral fraction becomes important in governing retention in soils with a high content of Fe, Mn, and Al oxides or with a low organic matter content, as in subsoils (Germon and van Driel, 1984). Because of the common occurrence of hydrous metal oxides of Fe and Mn as surface coatings, these mineral oxides can exert a chemical activity far out of proportion to their total concentrations (Jenne, 1968). The hydrous oxides are reduced at low pH and redox potential levels. Manganese begins to come into solution at $E_h = +300$ mV, with most of the reducible Mn dissolved by $E_h = +100$ mV. Very little Fe is reduced until nearly all the available Mn is reduced (Jenne, 1968). Thus, trace metal retention by these oxides is affected by redox potential.

The retention of heavy metals (Pb, Cd, Zn) by hydrous ferric oxides is favored at higher pH values (Gadde and Laitinen, 1974). The retention of these metals by hydrous Mn oxide increased linearly in the pH 2 to pH 6 range (Gadde and Laitinen, 1974). Swallow et al. (1980) stated that the removal of a metal from solution by hydrous oxides can be approximately predicted under all concentrations and electrolyte conditions by a constant which is only a function of pH. If metals are present in solution when precipitation occurs, they will be incorporated into the ferric hydroxide precipitate (Lee, 1973).

The hydrous oxide surfaces are largely specific for the retention of heavy metal ions. Kinniburgh et al. (1977) concluded that Cd and Zn were specifically adsorbed by Fe and Al hydrous oxides based on the evidence that retention increased with increasing pH below the zero point of charge (zpc) of the oxides. Since Ni^{2+} and Cu^{2+} were not released from the soil when the pH was lowered below the zpc, Murray et al. (1968) concluded that the metals were specifically adsorbed. Khalid et al. (1978) reported that Cu, Cd, Zn, and Pb were retained by hydrous oxides of Fe and possibly Mn in the sediments. Of this group, Cd was retained the least by the oxides. They also reported that the metals may be released as pH decreases under oxidizing conditions due to H^+ displacement. Nair and Cottenie (1971) concluded that there was convincing statistical proof that amorphous Fe oxides, possibly present as a surface coating of fine particles, retained a large portion of the Cu, Pb, and Zn in their investigation.

Gulens et al. (1979) reported that As retention by hydrous oxide surfaces varied with the oxidation state of As, the redox environment, and/or pH of the eluting water. Arsenate retention was predominately by the poorly crystalline hydroxy-Fe and hydroxy-Al compounds of recent weathering (Livesey and Huang, 1981). Ferric oxide retained As(III) while Fe(III) oxide and Mn oxide retained little As(V) (Oscarson et al., 1981). Fuller (1978) reported that anion metal retention correlated more strongly to free Fe oxides than surface area. He also reported that As retention could be predicted at the 95% confidence level by an equation including percent clay, surface area, and percent Fe oxides as the independent variables.

As a soil changes from an oxidizing to a reducing condition, the soluble level of metals may increase (Fuller, 1980; Bates, 1980), or decrease (Page and Pratt, 1975), depending on the presence or absence of sulfides and other redox active components in the system and an interaction between these processes. When hydrous Fe- and Mn-oxides are reduced, the heavy metals which are coprecipitated with or retained by the oxides should be released (Thibodeaux, 1979), and soluble levels may increase if other processes do not come in to play immobilizing metals. Upon oxidation of a strongly reduced sediment or soil, sulfide is converted to elemental sulfur which is then converted to sulfate (Patrick et al., 1977) making the metals more available. Often, especially in sediments, there may not be a great change in soluble levels of some metals upon a redox change because of the complimentary nature of the immobilizing processes.

Examining the effects of pH and redox potential on the various chemical forms of heavy metals in sediments, Gambrell et al. (1976, 1980) detected little if any dissolved Pb at any pH-redox potential combination. Exchangeable labelled Pb was detected under moderately acid pH conditions. The recovery of labelled Pb in the exchangeable fraction was influenced more by pH than oxidation intensity. Half or greater of the labelled and the potentially reactive indigenous Pb was recovered by DTPA extraction. Increasing the redox potential from -150 mV to +50 mV resulted in an increase in DTPA extractable Pb at pH 5.0 and pH 6.5. However, subsequent increases in oxidation resulted in little change to moderate decreases. The recovery of Pb associated with oxides increased with increases in redox potential (-150 mV to +500 mV) and was less affected by pH. Approximately half of the labelled Pb was recovered in this reducible

fraction under oxidizing conditions. Therefore, the researchers concluded that most of the labelled Pb and approximately half of the total indigenous Pb were recovered in potentially available forms under oxidizing and reducing conditions by their sequential chemical fractionation procedure. However, 5% or less of the Pb was present in the readily available soluble and exchangeable forms at any pH-redox combination.

Khalid et al. (1981) proposed that redox potential and pH may be the most important physicochemical parameters influencing Cd transformations and availability to biota. For this reason, Khalid et al. (1979, 1981) varied Eh and pH in their study of Cd retention by sediments. The recovery of ^{109}Cd in a soluble form was negligible under reduced conditions (-150 mV and 0 mV) at pH 5.0 and pH 6.5, probably due to sulfide precipitation (total sulfide > 500 $\text{mg}\cdot\text{kg}^{-1}$ solids). Essentially all of the ^{109}Cd was associated with sediment solids under slightly alkaline and near-neutral, oxidizing conditions. The researchers found a marked increase in ^{109}Cd solution concentrations as the reduced suspensions were oxidized, and this effect of enhanced Cd mobility was in the order of pH 5.0 >> pH 6.5 >> pH 8.0. Exchangeable Cd was negligible in the reduced to moderately reduced sediment at pH 5.0 and pH 6.5, but was detected in increasing amounts as the oxidizing intensity increased at these pH values. Redox potential had no effect on Cd release from the sediment at pH 8.0 where up to 200 $\text{mg}\cdot\text{kg}^{-1}$ of Cd was present. Chelated (DTPA-extractable) Cd recovery increased with increasing oxidation intensity at pH 8.0 and pH 6.5. No trend in DTPA-extractable ^{109}Cd was observed at pH 5.0. Reducible Cd, i.e., Cd adsorbed by or coprecipitated with hydrous oxides of Fe and Mn, was not significantly affected by

changes in pH or redox potential levels. The recovery of insoluble organic-bound ^{109}Cd was highest under strongly reduced sediment conditions and then decreased with increasing oxidation potential at all pH levels studied. In conclusion, the authors found that under alkaline conditions, essentially all of the ^{109}Cd extracted was associated with the potentially available chelated, reducible, and insoluble organic-bound fractions and was little affected by changes in redox potential. A change from alkaline to acidic pH under moderately oxidized to well-oxidized conditions resulted in ^{109}Cd transformations from the potentially available forms to more mobile and readily available dissolved and exchangeable forms.

Reddy and Patrick (1977) found that as the redox potential of the sediment suspension decreased, the percentage of Cu that remained in solution also decreased. Elsewhere, reducible Cu has been reported to increase with increasing oxidation intensity, becoming 50% of the total Cu in oxidized sediment (Gambrell et al., 1976).

Gambrell et al. (1976, 1980) determined that Zn solubility was strongly pH dependent with greatest levels found at pH 5.0 in Gulf Coast sediments. This soluble Zn was most likely present in the free cationic form. Exchangeable Zn, like dissolved Zn, was greatest at pH 5.0 and decreased to levels undetectable by flame atomic absorption at pH 8.0. Exchangeable Zn was substantially lower under strongly reducing conditions (-150 mV) than under more oxidized conditions at pH 5.0 and pH 6.5. Water-soluble Zn responded similarly. Recovery of Zn was greater for the reducible form than for the other chemical forms studied. Therefore, it was concluded that adsorption on or coprecipitation with hydrous oxides was the major process immobilizing potentially available Zn.

Sims and Patrick (1978) examined the changes in the chemical forms of Zn and Cu as pH and redox potential were altered. They found less water-soluble Zn at low pH or Eh values, while less water-soluble Cu was found at low pH and high Eh levels. More exchangeable Cu and Zn were detected at low pH and Eh values. Zinc and Cu were associated with Fe and Mn oxides and hydroxides more at high pH and Eh levels. They determined that Zn and Cu were associated with the organic fraction more at low pH and Eh levels because Zn and Cu retention on both anionic and cationic resins decreased with the degree of soil reduction. Zinc and Cu recovery in the residual fraction was greatest at high pH and Eh values, as was seen for the reducible fraction. Zinc in the residual and oxalate fractions was transformed into the organic fraction as the redox potential decreased. Copper in these two fractions was transformed into both the organic and water-soluble fractions as the redox potential decreased.

Lion et al. (1982) reported that most of the Cd, Cu, and Pb in sediment samples from the South San Francisco Bay estuary was associated with the operationally defined organic and/or metal (Fe, Mn) oxide surface coatings. Fifty percent of the extractable Cd and 65% of the extractable Cu were associated with the organic phases, while 70% of the extractable Pb was associated with the Fe and Mn oxides.

Gerritse and van Driel (1984) calculated the exchangeable fraction of Pb to be in the range of 1% to 5%, while that of Cd, Zn, and Cu was in the range 10% to 50%. Shuman (1979) reported that the average relative amount of Zn in fractions of ten soils followed the order: residual clay > Fe oxides > residual sand \geq residual silt \geq organic matter > exchangeable; for Cu, the order was: organic matter > residual clay > residual silt > residual sand > Fe oxides > exchangeable. Residual sand,

silt, and clay refers to the fact that the metals were extracted first for exchangeable, organic matter, and Fe oxides fractions then the residue was separated into sand, silt, and clay size particles which were totally dissolved and analyzed for the metals.

Solution composition will also greatly affect metal retention and movement. In most of the cases studied by Benjamin and Leckie (1982), addition of Cl^- or SO_4^{2-} reduced Cd retention indicating that chloro- and sulfato- complexes are retained less strongly by the soil than are uncomplexed Cd ions. Garcia-Miragaya and Page (1976) found that Cd retention decreased in the order (same ionic strength): ClO_4^- (perchlorate) $> \text{SO}_4^{2-} > \text{Cl}^-$. Brown (1979) stated that the formation of complexes of Pb with various anions such as Cl^- , F^- , CO_3^{2-} , HCO_3^- , and OH^- increased the concentration of Pb in natural waters preventing Pb from taking part in other chemical reactions, primarily adsorption, which would lower the solution concentration.

Knox and Jones (1979) reported that all of three sanitary landfill leachates tested were able to complex Cd to some extent, although their ability to do so varied, and in some cases might well have been insufficient to greatly affect metal removal from solution. The reaction between Cd and leachate appeared to be mono-nuclear and predominately a 1:1 complex formation. Although fatty acids were the most important complex-forming fraction in one leachate studied, other organic compounds, such as fulvic acid, were important in the other two leachates.

Boyle and Fuller (1987) reported that the total organic carbon (TOC) and total soluble salts (TSS) content of municipal solid waste leachate were more important in determining Zn attenuation behavior than soil

characteristics. In general, Zn migration through soil was facilitated by higher TOC and TSS levels in the leachate.

Sheets and Fuller (1986) studied the effect of 2-propanol and ethylene glycol on Cd movement through soils. Soils retained less Cd from ethylene glycol than from water. Cadmium retention decreased with increasing 2-propanol concentration in a sand and sandy loam but increased with increasing 2-propanol concentration in a clay. Schnabel and Fuller (1984) reported more rapid breakthrough of Cd and Zn in soils leached with alcohol solvents than soils leached with water. Nickel mobility was less affected by the alcohol solvents. Thus, the degree of metal immobilization or transport depends upon an interaction between soil properties, the amount of metals present, and the properties of the leachate phase with which the metals are associated.

Sequential extraction methods, whereby metals associated with specific soil and sediment mineral phases are determined, provide a means of assessing the solid phases controlling metal retention in soils and sediments (Pickering, 1981; Salomons and Forstner, 1984). However, sequential extraction methods suffer from a number of problems including: (1) lack of selectivity during extraction in which weakly retained metals on other phases are extracted during selective dissolution of a particular phase, (2) incomplete extraction, and (3) readsorption during extraction in which metals solubilized during selective dissolution of a particular phase are readsorbed onto other phases. The first error overestimates amounts of metals associated with a particular phase, whereas the latter two errors underestimate the amounts of metals associated with a particular phase (Pickering, 1981). Thus, sequential extraction methods must be regarded as semi-quantitative. Despite the errors associated with

such methods, they still offer vital clues as to the behavior of metals in soils and sediments.

RESEARCH APPROACH

Field and laboratory studies were conducted to examine factors affecting the mobility of metals in subsoils. The experimental approaches for these studies are summarized below.

Field Studies

The objectives of the field studies were to determine the distribution and forms of trace and toxic metal contaminants in the subsoil at sites with known or suspected potential for groundwater contamination. Soil cores were taken to a depth of 2-3 m at the sites with a hydraulically-driven 4.75-cm stainless steel coring tube. The cores were sectioned with depth in the field, stored in plastic bottles, and then returned to the lab for analyses.

The field studies were planned to be coordinated with laboratory studies in terms of the soil materials studied and the contaminants present. Assistance in locating and getting access to contaminated field sites was obtained from the U.S. EPA, the U.S. Air Force, the Louisiana Department of Environmental Quality (DEQ), and the Louisiana Department of Transportation and Development (La. DOTD).

Though considerable effort was expended in identifying the sites, securing authorization for access to the sites, sampling, and analyzing samples, this effort was only partially successful because clear indication of high metals contamination was not apparent in core samples

from several of the locations. Two of the most promising sites in Louisiana were unavailable, and alternative sites were selected.

Laboratory Studies

Three laboratory studies were conducted to examine factors affecting metals movement in subsoils. These included batch and column transport studies. The first batch study focused on retention of Cd and Pb by five subsoil materials with and without the presence of four simulated co-wastes (0.005M $\text{Ca}(\text{NO}_3)_2$, municipal landfill leachate, acidic metals waste, oil field waste). The term co-waste refers to a waste material that may be present at a disposal site possibly facilitating the mobility of metals. Calculations of adsorption coefficients and correlation analyses were used to examine the effects of specific soil properties and the presence of co-wastes on metal retention. Because of the importance of soil redox potential on the environmental chemistry of metals, a second batch equilibration study was performed with two levels of Cd and Pb and the same co-wastes and subsoil materials, but under different purge gases simulating aerobic and anoxic conditions in the subsoil materials. The column transport study included two soil materials receiving the four co-waste solutions.

The objectives of this project were as follows:

(1) To identify soil physical and chemical properties regulating the mobility of metals in subsurface soil materials. This research focused on subsoils between the contaminated soil at or near the surface and the groundwater. Much has been published on the mobility and biological availability of metals in surface soils and sediments. Factors affecting

the mobility of metals from waste disposal sites in subsoils has received comparatively little attention.

(2) To show for Cd and Pb the important interactions between metal concentrations, waste mixtures, and soil properties in regulating the mobility of metals. It is well documented that all metals do not respond identically to mobilization/immobilization processes in soil. In addition to soil properties and the particular metals present, there are two other important factors that may influence the mobility of metals in subsoils: (1) the concentrations of metals present, and (2) the presence of other types of wastes that may influence the mobility of metals. These two factors have particular relevance to waste sites presenting a threat to groundwater and were considered in planning this study. These differences in the environmental chemistry of metals were studied in the context of hazardous waste disposal sites which represent the greatest potential threat to groundwater contamination by metals.

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CHAPTER 2

THE DISTRIBUTION AND ENVIRONMENTAL CHEMISTRY OF LEAD
IN SOIL AT AN ABANDONED BATTERY RECLAMATION SITE

ABSTRACT

The distribution and environmental chemistry of Pb in soil was determined at a former battery storage site near Pontchatoula, Louisiana, where the soil was contaminated with acid and Pb. Highest concentrations of Pb were found at the soil surface and at the top of the groundwater table with lower values in between. The elevated concentrations of Pb at the groundwater table were associated with higher pH and Mn oxide levels in this part of the profile. The percentages of Pb recovered with different extractants in a sequential fractionation scheme varied with depth suggesting possible changes in the form of Pb with depth. Water-soluble Pb was negatively correlated to pH. Most of the extractable Pb forms were correlated with Mn oxide at depth. Long-term laboratory release studies showed that Pb could be mobilized in this soil and supported the findings that Pb has moved through the profile at this site and may have moved laterally with groundwater.

INTRODUCTION

The movement of metals in soils contaminated with metal-enriched waste materials is dependent upon the physical and chemical properties of the soils and the characteristics of the waste materials. A battery reclamation facility, such as Pontchatoula Battery, Pontchatoula, Louisiana, provides circumstances where soil and groundwater contamination by metals, particularly lead (Pb), may occur, and where the presence of a waste material other than metals may accelerate metal movement towards groundwater. If old battery cases are stored as a pile on the ground prior to Pb recovery, spilled sulfuric acid can facilitate the movement of the Pb contained in the batteries through the soil. The Sapp Battery site in Jackson County, Florida (Watts, 1984) is very similar to Pontchatoula Battery in that old battery casings were disposed of on site without prior cleaning. This has led to contamination of soil, shallow groundwater, and the Floridan aquifer with Pb.

Initial forms of Pb deposited at battery reclamation sites include Pb, PbO_2 , and PbSO_4 (Watts, 1984). Although many Pb minerals can potentially control Pb solubility in soils (Lindsay, 1979), Pb retention in soils beneath the A horizon (topsoil) is most likely controlled by coprecipitation with other mineral phases and sorption onto metal oxides, particularly Fe and Mn oxides (Hem, 1978, 1980; Kinniburgh and Jackson, 1981). Changing redox conditions (alternating oxidizing/reducing conditions) within the soil profile can lead to alternating precipitation and dissolution of Fe and Mn oxides which will immobilize or mobilize associated Pb. This process may be important in soils with seasonally fluctuating shallow water tables which are often found in Louisiana soils.

The objectives of this study were: (1) to determine the distribution of Pb in soil cores at a battery reclamation site; (2) to determine the quantities of Pb associated with specific mineral phases using a sequential extraction scheme; (3) to relate Pb distribution to soil properties; and (4) to determine long-term Pb release from Pb-contaminated soil under alternating oxidizing/reducing conditions.

MATERIALS AND METHODS

Site Description

Pontchatoula Battery, located near Pontchatoula, Louisiana, reclaimed Pb from old automobile and marine batteries. The plant last operated in October, 1981. Contamination of the site occurred as a result of storage of the batteries in large piles prior to reprocessing. Piling batteries with no attention to keeping them in an upright position to avoid spillage and cracking of battery cases resulted in acid and acid-solubilized Pb contamination of the soil. Though most of the batteries have been removed, further clean-up of the site has not been completed due to a lack of funds.

The largest portion of the site consisted of a battery case pile 100 m by 30 m by 10 m high (Figure 1). Two neutralization ponds, a neutralization tank, a caustic tank, and a storage tank were located at the northern end of the site near a swampy area.

There was no vegetation on the exposed soil at the site at the time of our sampling. Surrounding the site was a ring of dead trees. To the west of the site was a second battery reclamation site.

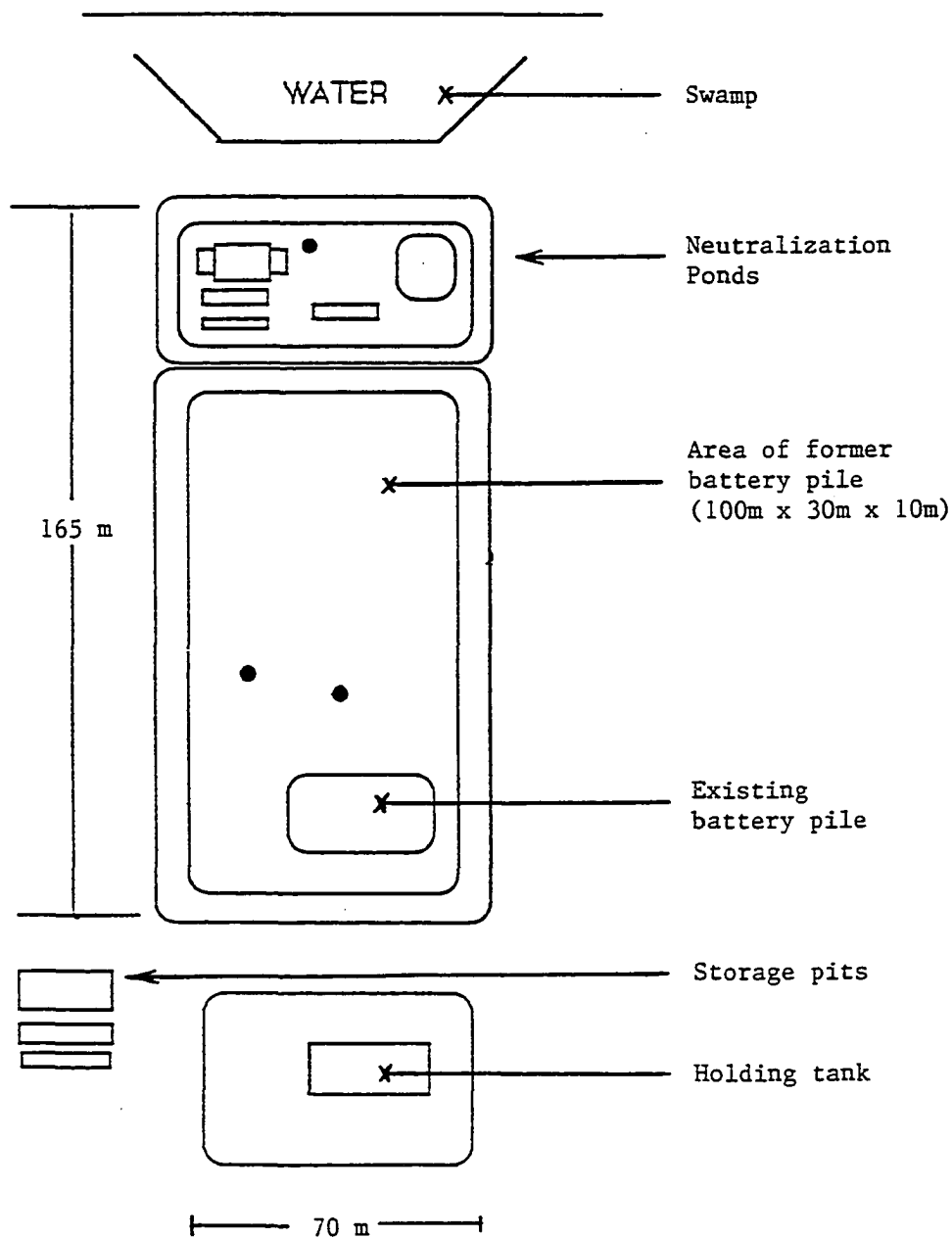


Figure 1. Location of core sampling sites at Pontchatoula Battery, Pontchatoula, Louisiana.

Previous investigations by the Louisiana Department of Environmental Quality (LA. DEQ) indicated high levels of total Pb in the soil to a depth of 1.3 m (up to 37,000 mg•kg⁻¹). Surface water analysis showed that some outflow occurred into local streams with soluble Pb levels up to 17.7 mg•L⁻¹ and surface water pH as low as 1.4. Although no monitoring wells had been installed, it was hypothesized that ground water contamination may have occurred due to the shallow ground water at the site, the sandy soil, and the spilled acid from the batteries.

Sampling Procedures

Soil cores were obtained using commercial equipment that hydraulically presses a stainless steel core extractor tube (4.75 cm diameter) into the ground. Duplicate cores of 1-2 m length were taken at three locations within the contaminated site (Figure 1). The first pair of cores, A1 and A2, were taken approximately 2.5 m from the inside of a dike on the west side of the open plain. The second pair of cores, B2 and B3, were taken approximately half-way across the plain (former location of the large battery pile) and 15 m north of the existing case pile. Cores C1 and C2 were obtained from the northern end of the site, approximately 10 m south of the northernmost dike and 31 m east of the western dike. These cores were wetter than the others and had a H₂S odor. Background samples were obtained from a location near the road approximately 300 m south of the site.

After the cores were pulled to the surface, they were sectioned by depth and/or horizon and placed in 1-L plastic storage bottles. The samples were refrigerated upon return to the laboratory to preserve conditions found in the field.

The depth to the water table for the sampling sites were: A1 at 1.06 m; A2 at 1.2 m; B2 at 1.36 m; B3 at 1.36 m; C1 at 1.2 m; and C2 at 1.06 m. Groundwater samples were obtained from the A1 and C2 core holes using vacuum extraction. Surface water samples were obtained from the swamp at the north end of the site and from surface run-off near cores C1 and C2. Upon return to the laboratory, the samples were filtered through a 0.45 μ m membrane filter and analyzed for pH, then acidified and analyzed for elements of interest (particularly Pb) by ICP (inductively-coupled plasma) spectroscopy. Q

Soil Physical and Chemical Characteristics

To preserve field conditions, soil samples were not dried prior to analysis. Water content was determined by the water loss on drying at 105°C (Gardner, 1986) and was used to report all extraction concentrations on a dry weight basis. The pH of the samples was determined according to the method of McLean (1982). Cation exchange capacity (CEC) was determined by summing the major cations (Ca, Mg, Na, K, and Al) extracted with 0.1M BaCl₂ (adapted from Rhoades, 1982). Particle-size distribution was determined by the hydrometer method (Gee and Bauder, 1986). The Mn oxide content of the samples was measured using pH 2, 0.1M hydroxylamine hydrochloride (NH₂OH•HCl) (Chao, 1972). Amorphous Fe oxides were determined using 0.25M hydroxylamine hydrochloride-0.25M HCl (Chao and Zhou, 1983). Free (crystalline + amorphous) Fe oxides were determined using the dithionite-citrate-bicarbonate (DCB) method (Mehra and Jackson, 1960). Crystalline Fe oxides can be determined by subtracting the amorphous Fe oxide content from the free Fe oxide content.

The soil at the site has not yet been classified.

Chemical Forms

The soil samples were extracted to determine selected chemical forms of Pb using the sequential fractionation scheme outlined in Figure 2. This design is not based on any particular scheme in the literature, but is similar to several used by other investigators (Pickering, 1981; Salomons and Forstner, 1984). The scheme consists of extracting Mn oxides, amorphous Fe oxides, and free Fe oxides in sequence preceded by extractions with a neutral salt (BaCl_2) and a chelating agent (EDTA) to determine weakly and strongly sorbed Pb. The extractants in the sequential fractionation scheme were intended to extract Pb associated with the following chemical phases in soils: (1) 0.1M BaCl_2 - weakly sorbed and exchangeable Pb; (2) 0.05M EDTA - strongly sorbed Pb; (3) pH 2, 0.1M $\text{NH}_2\text{OH}\cdot\text{HCl}$ - Pb associated with Mn oxides; (4) 0.25M $\text{NH}_2\text{OH}\cdot\text{HCl}$ -0.25M HCl - Pb associated with amorphous Fe oxides; and (5) DCB - Pb associated with free Fe oxides (crystalline Fe oxides + amorphous Fe oxides not extracted by extractant (4)). The BaCl_2 and EDTA extractants do not dissolve a particular mineral phase, thus Pb sorbed to a variety of mineral phases including metal oxides can be extracted with these extractants. The metal oxide extractants extract strongly sorbed Pb not extracted by the BaCl_2 and EDTA as well as Pb coprecipitated with the metal oxides.

The water-soluble, acid-extractable, and total Pb in the soil samples were determined on separate soil aliquots using the methods listed in Table 1. Separate soil aliquots were used for these extractions because: (1) water-soluble Pb levels were typically low, requiring a larger sample than that used in the sequential extraction scheme; (2) the 0.1N HCl does not extract a specific phase but extracts potentially

SEQUENTIAL FRACTIONATION SCHEME

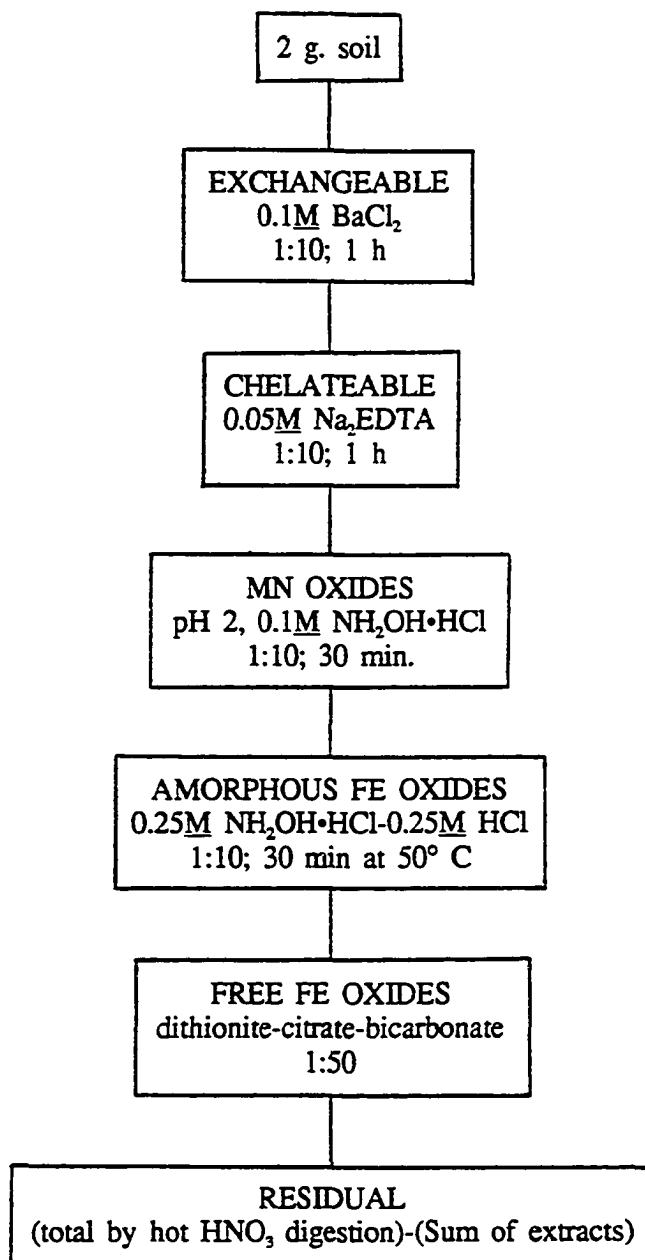


Figure 2. Sequential fractionation scheme used to determine the distribution of Pb in the soil at Pontchatoula Battery.

Table 1. Methods for determining soluble, acid extractable, and total Pb.

Fraction	Extractant	Soil/Extractant Ratio	Extraction Time
H ₂ O-soluble	0.005M Ca(NO ₃) ₂	1:10	16 hr
Acid-extract.	0.1M HCl	1:10	1 hr
Total metal	Hot HNO ₃	1:20	6 hr

available Pb in several phases; and (3) difficulty in determining the low levels of residual Pb in soil after the fractionation scheme. The residual fraction was determined by subtracting the sum of Pb extracted in the sequential fractionation from the total Pb determined on a separate aliquot. A dilute salt solution (0.005M $\text{Ca}(\text{NO}_3)_2$) was used in place of deionized water for the "water-soluble" phase to better mimic the soil solution and to facilitate filtration (Amacher, 1984).

Long-Term Release of Pb

To determine if Pb is being released over time and if this release is affected by changing redox conditions, 0.005M $\text{Ca}(\text{NO}_3)_2$ was added to selected contaminated soil samples from the site at a soil/solution ratio of 1:10 and continuously shaken on a reciprocating shaker at $140 \text{ osc} \cdot \text{min}^{-1}$. The soil/solution mixtures were purged daily with air (designated as O_2 in text and figures) for two weeks, then with Ar for two weeks, then again with air for two weeks, then with Ar for two weeks using the experimental setup described in Chapter 6. The suspensions were sampled twice weekly, filtered, and analyzed for elements of interest by ICP. The redox potentials of the samples were determined at sampling using a platinum (Pt) electrode and a Ag/AgCl reference electrode. The study was run in duplicate (subsamples A and B).

The samples chosen for this study contained high levels of total Pb. Two samples were chosen from core A2: A2-1 (0.15 m depth) and A2-5 (1.2 m depth); one from core B2: B2-7 (1.67 m depth); and two from core C2: C2-1 (0.3 m depth) and C2-5 (1.4 m depth).

RESULTS

Water Analysis

The pH and Pb content of the water samples are presented in Table 2. The pH of the groundwater sample from core A1 was less than the corresponding soil pH (Figure 3), while the pH of the water sample from core C2 was similar to the corresponding soil pH (Figure 3). Surface run-off from the site near core C1 and C2 had a low pH (pH 3.4). The standing water in the swamp had a lower pH than the running water. These low pH values indicate the presence of waste acid still in the soil at the site. Since battery storage activity ceased several years ago and most of the batteries have been removed, it is likely that in years past, surface and subsurface waters were even more acidic than measured during the time of this project.

The concentration of Pb in all water samples exceeded the EPA criteria of $0.050 \text{ mg} \cdot \text{L}^{-1}$ for domestic water supply (USEPA, 1976), which is given here simply for comparison purposes. The concentration of Pb in the water samples was negatively related to the pH of the sample. Lead was highest in the surface run-off sample, which had the lowest pH, and lowest in the running water by the swamp, which had the highest pH. This reflects the role of the acid present in solubilizing the Pb and contributing to its movement.

Soil Physical and Chemical Characteristics

The soil physical and chemical characteristics determined for this study included pH, cation exchange capacity (CEC), particle-size distribution, Mn oxides, amorphous Fe oxides, and free Fe oxides. The

Table 2. Results of water analyses at Pontchatoula Battery.

Sample	pH	Pb, mg•L ⁻¹
<hr/>		
C2 groundwater	3.76	0.899
A1 groundwater	3.96	0.636
C runoff	3.40	5.976
Standing swamp water	4.96	0.308
Running swamp water	6.80	0.065

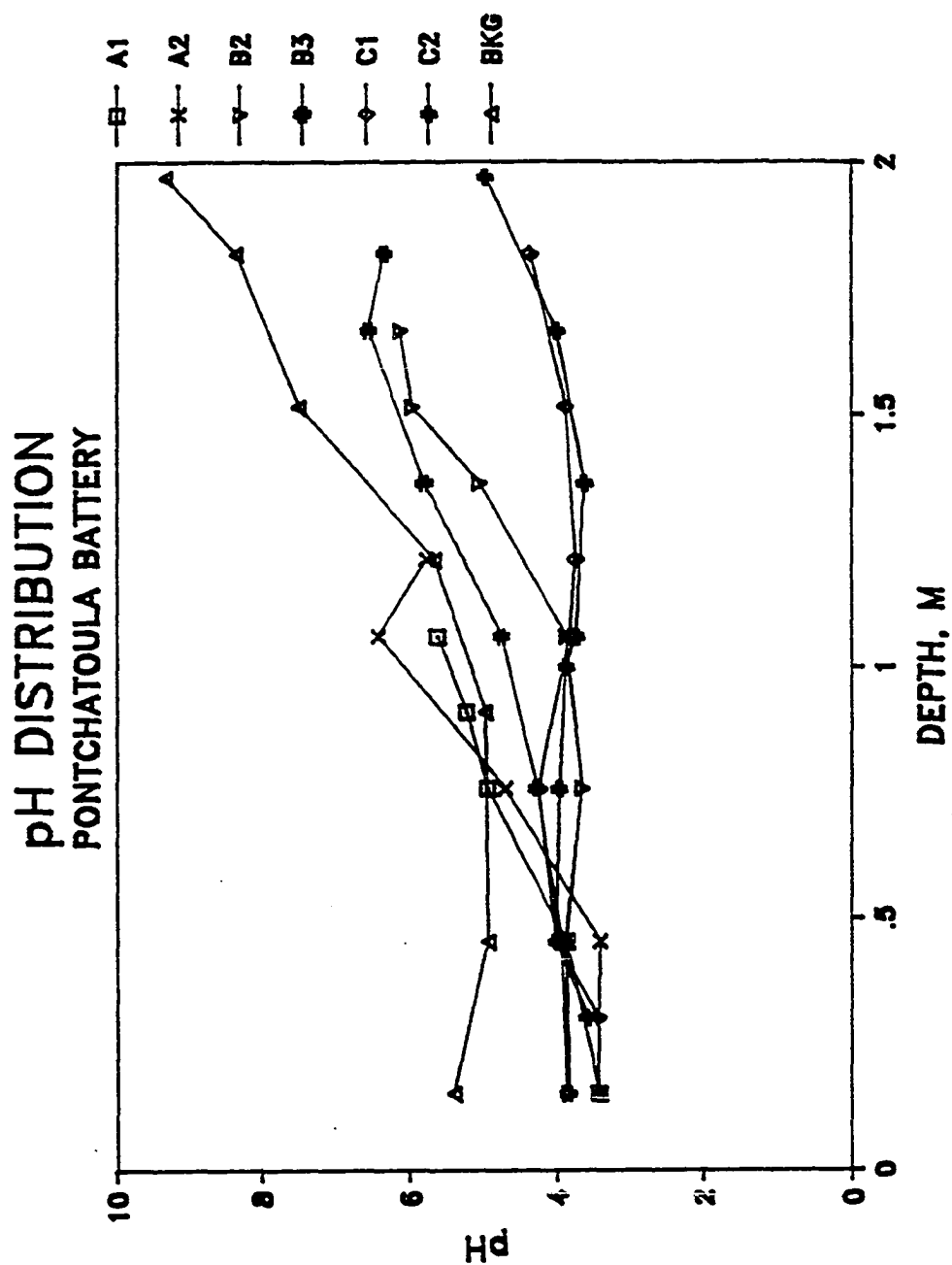


Figure 3. Soil pH with depth at Pontchatoula Battery.

soil organic matter content was not determined because we were primarily interested in the subsurface horizons where there is negligible organic matter present relative to surface soils. The distribution of soil pH is illustrated in Figure 3. The pH of the soil from the contaminated area was less than pH 4 at the surface, where spillage of acid in the battery piles was evident, and increased with depth. The pH of the A cores and the B1 core were highest at the top of the groundwater table. This may be due to a flushing and dilution effect of a fluctuating water table. The pH of the C cores was low and did not increase with depth. The pH did not exceed pH 6.5 in the cores from the contaminated zone. The pH of the background (Bkg) site was typically higher than that in the contaminated zone, rising above pH 8 at depths of 1.8 m or more. Since soil pH was never measured with depth at this site during plant operation and after its closure in 1981, it is not known whether the subsoil pH at the time of our sampling was as low as ever occurred at the site or whether several years of leaching has washed out some of the acid such that the profile is less acid now than in the past.

The CEC of this soil was low, less than $6 \text{ cmol}(+)\cdot\text{kg}^{-1}$ (Figure 4). For the B and C cores, the CEC was less than 1 at depths shallower than 1.5 m. For the A cores, the CEC increased more quickly with depth but dropped sharply at the groundwater table. The low CEC values are expected due to the sandy nature of the subsoil. However, displacement and leaching of the cations measured for CEC by sulfuric acid over the years may have contributed to an apparent low CEC artifact.

The soil texture ranged from a sandy loam to a loamy sand. The percent sand was typically greater than 30% (Figure 5). For the A1 core, sand percent increased with depth. For the A2 core, sand decreased to the

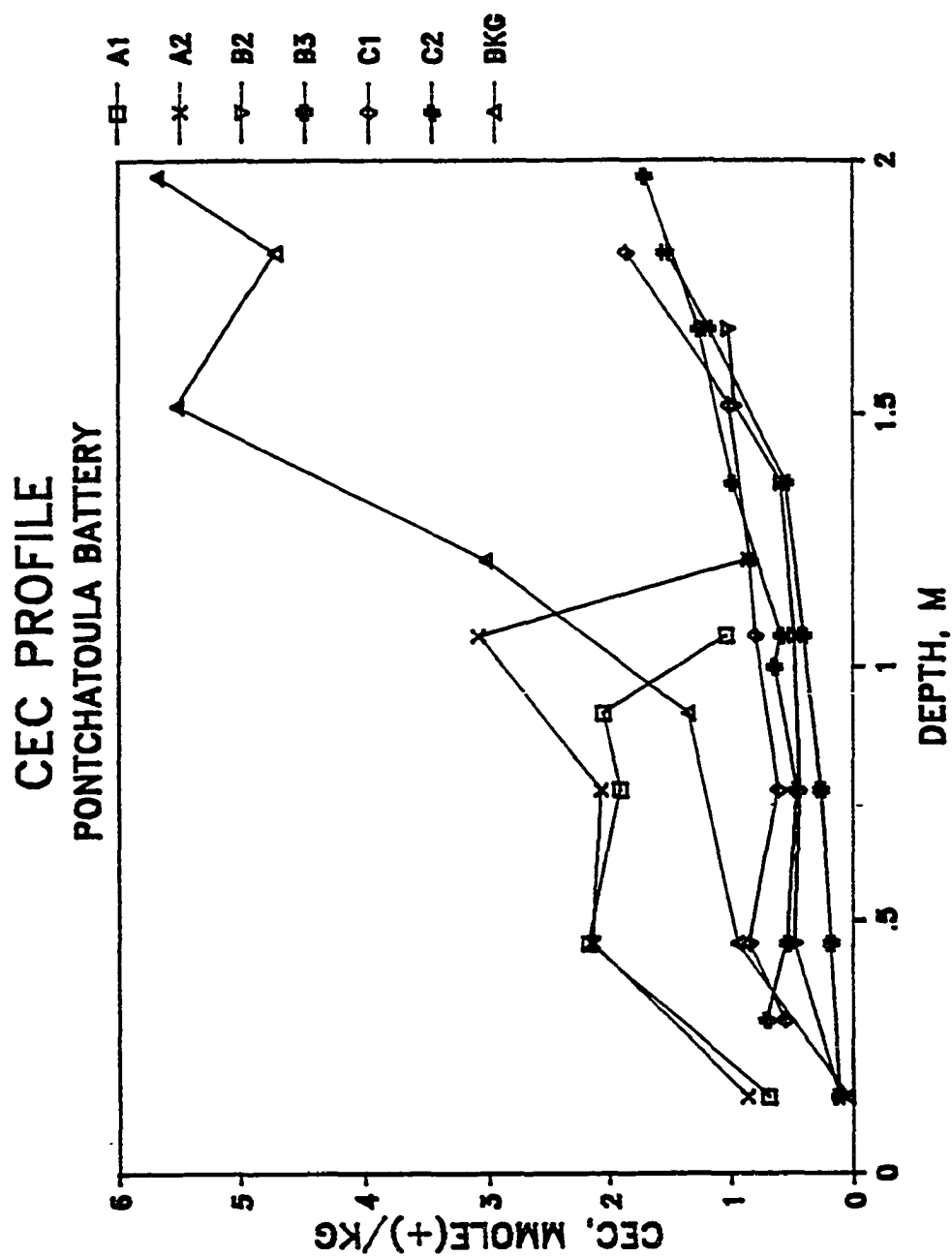


Figure 4. Cation exchange capacity (CEC) with depth at Pontchatoula Battery.

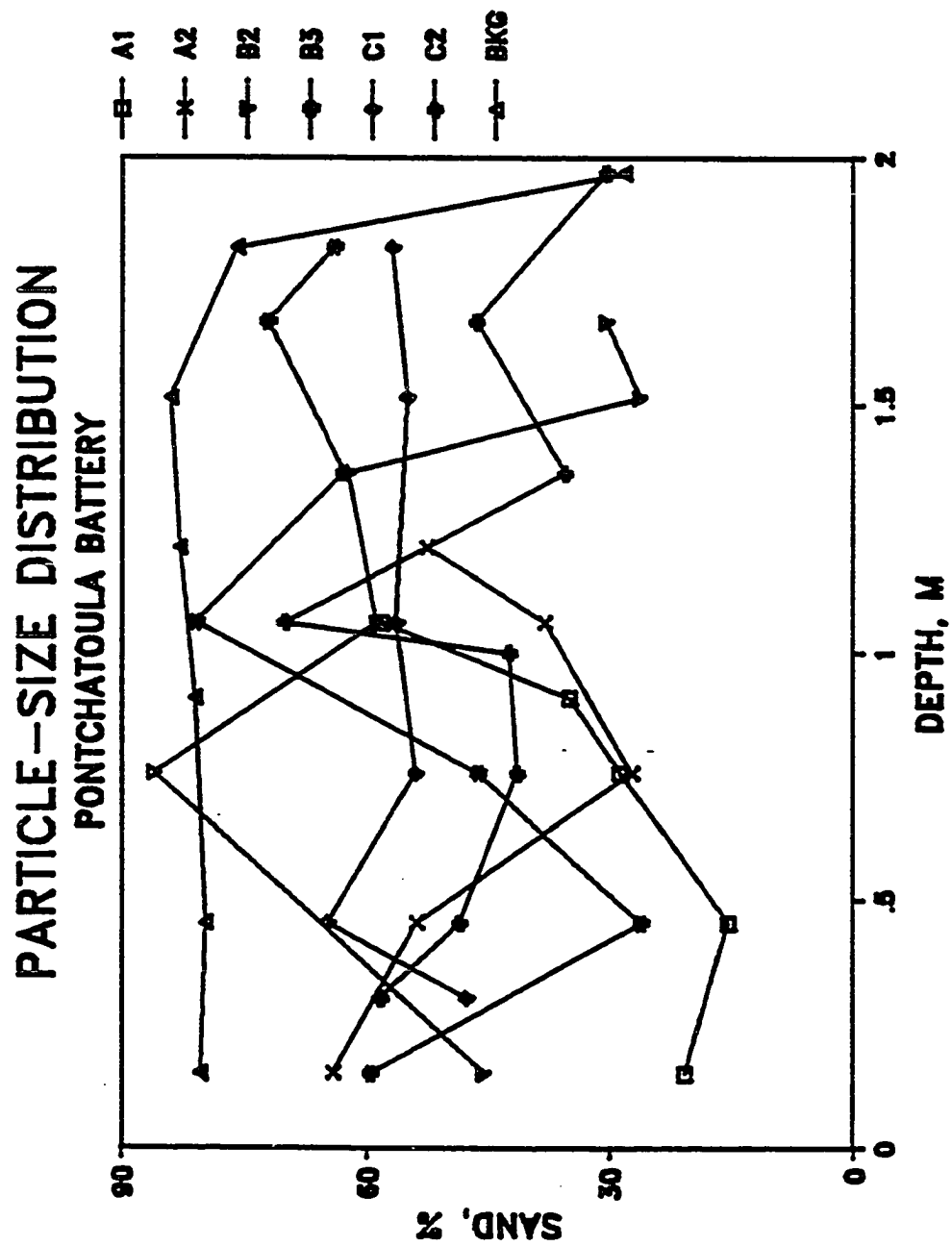


Figure 5. Sand content with depth at Pontchatoula Battery.

0.75 m-depth, then increased. For the B cores, the percent sand peaked near 1 m. Thus, a sand lens occurs at the site and corresponded to the top of the groundwater table at the time of sampling. The sand percentage did not fluctuate as much for the C cores. The sand content in the background core was high but decreased rapidly after 1.7 m.

The percent clay was less than 50% and usually less than 30% (Figure 6). Because of the sandy nature of the soil, it would be expected that this soil would not be able to retain much metal.

The Mn oxide content of the soil was very low, less than 0.05% MnO_2 (Figure 7). It was especially low in the C cores and in the Bkg core. The Mn oxide content in the A and B cores peaked at approximately 0.45 m then decreased with depth. There was a second peak in Mn oxides at the groundwater table in the A cores.

The amorphous Fe oxide content of the soil was very low, less than 0.25% Fe_2O_3 (Figure 8). The Fe oxide content was variable with depth.

The free Fe oxide content, like the other oxides, was very low, less than 0.25% Fe_2O_3 (Figure 9). The free Fe oxide content was variable with depth. There was evidence of mottles in the cores indicating alternating periods of oxidation and reduction, possibly due to a rising and falling groundwater table.

The ranges of the soil characterization data from Cores A, B, and C in contaminated areas are summarized in Table 3.

Chemical Forms

The samples were also extracted to determine the chemical forms of the metals. The "water-soluble" phase was determined by extracting with 0.005M $\text{Ca}(\text{NO}_3)_2$. This dilute salt solution was used to maintain an ionic

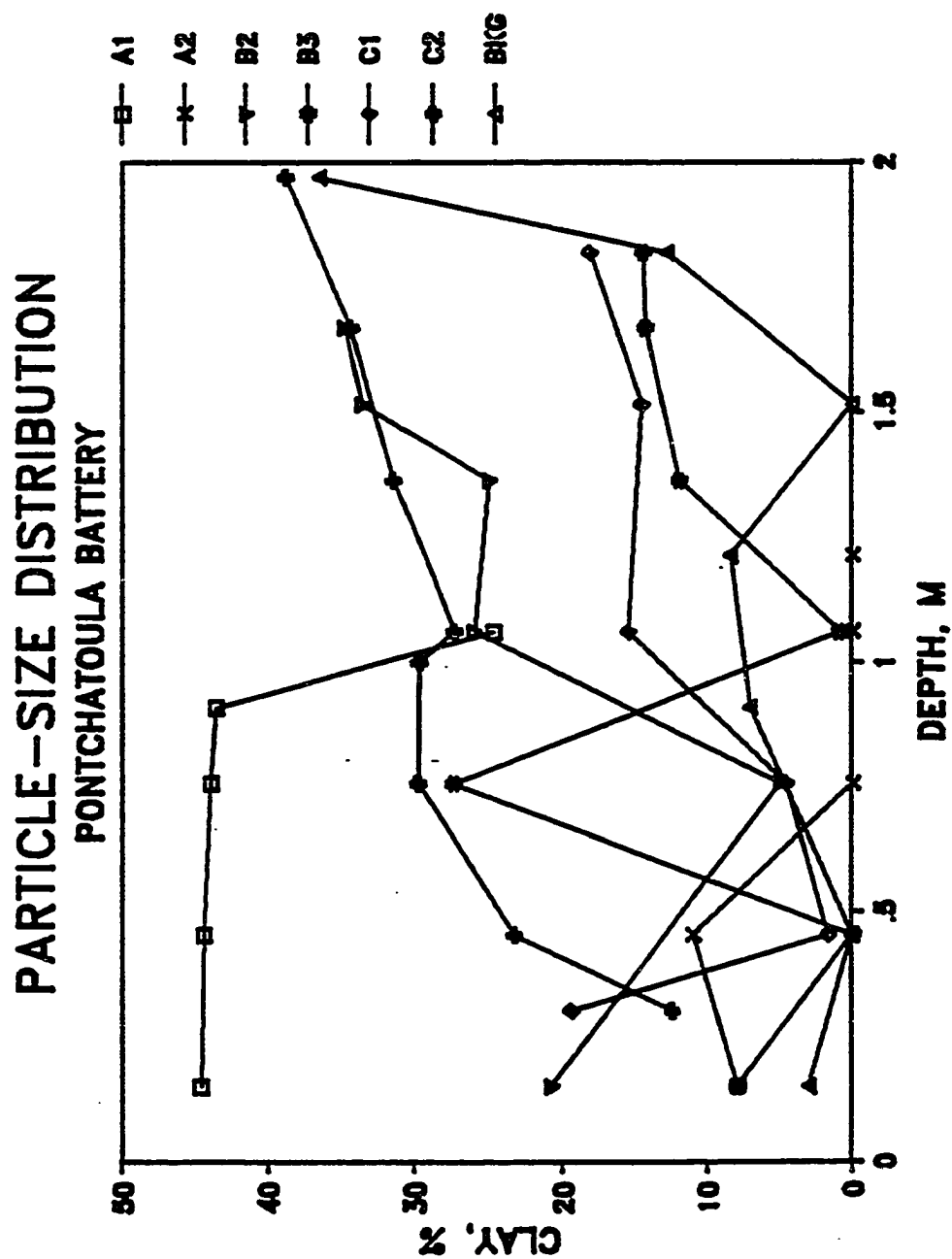


Figure 6. Clay content with depth at Pontchatoula Battery.

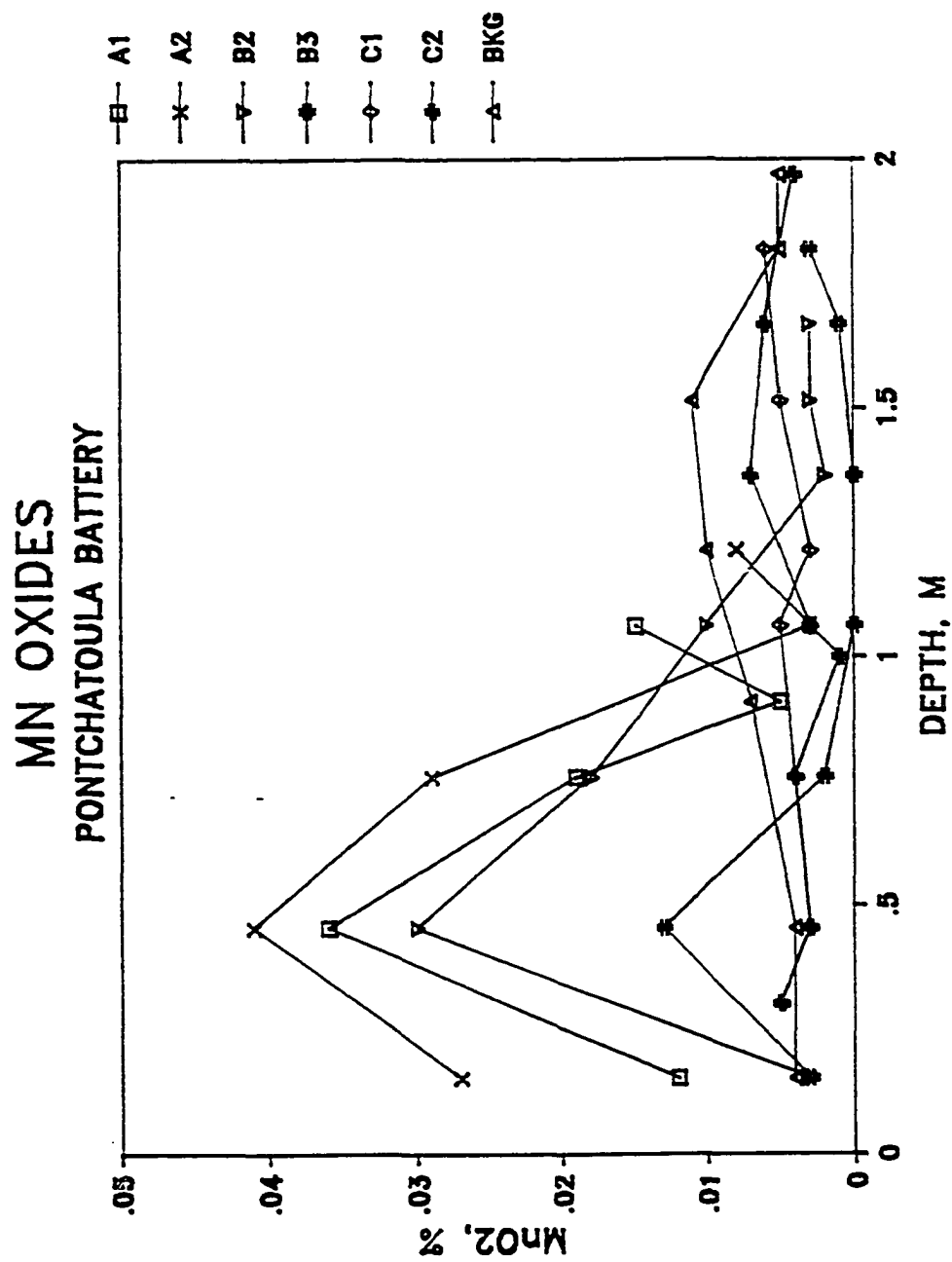


Figure 7. Manganese (Mn) oxide content with depth at Pontchatoula Battery.

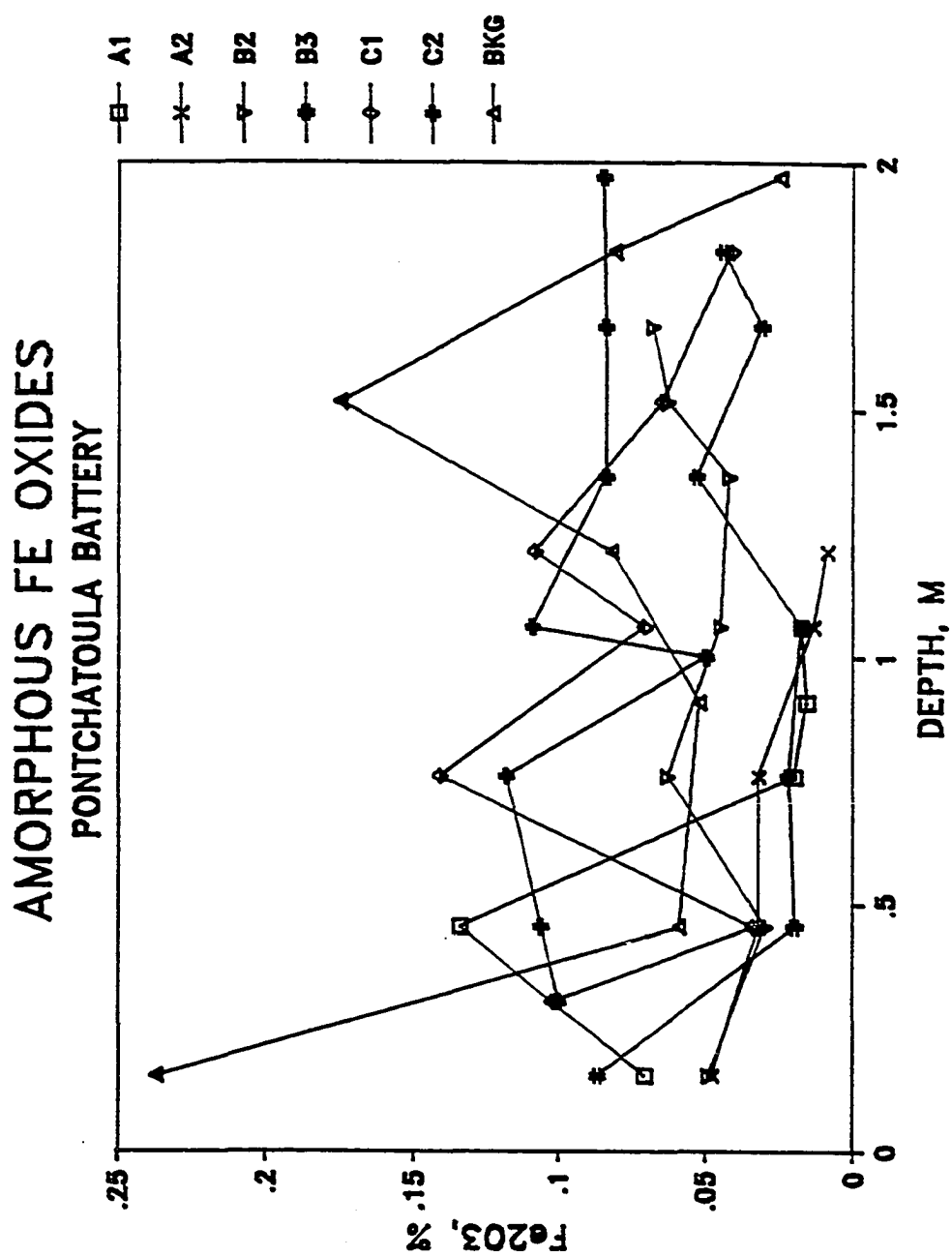


Figure 8. Amorphous iron (Fe) oxide content with depth at Pontchatoula Battery.

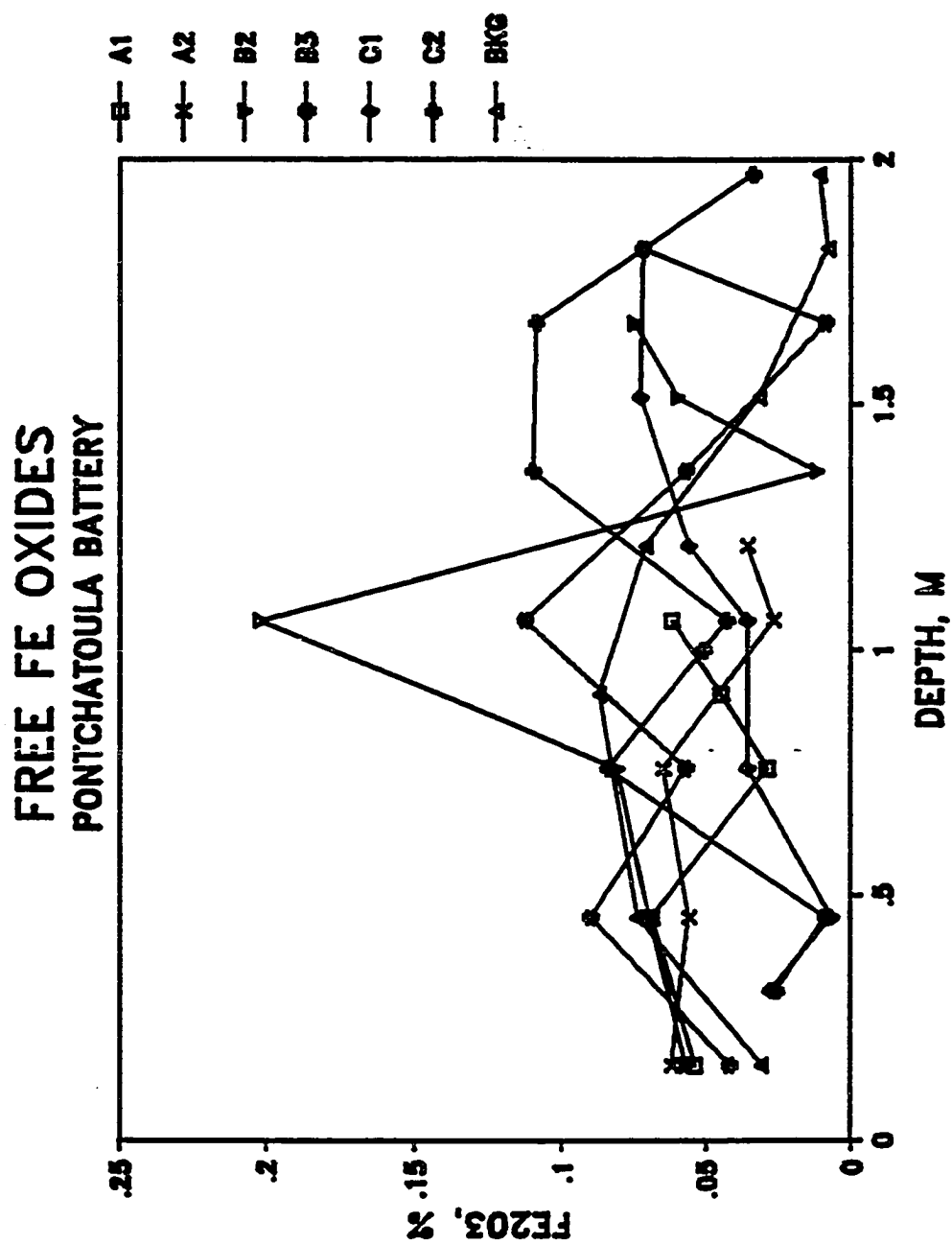


Figure 9. Free iron (Fe) oxide content with depth at Pontchatoula Battery.

Table 3. Soil characterization data from Pontchatoula Battery.

Property	Range in Contaminated Areas
<hr/>	
Soil pH	3.44 - 6.58
CEC, $\text{cmol}(+)\cdot\text{kg}^{-1}$	0.12 - 3.09
Mn oxides, % MnO_2	0.000 - 0.041
Amorph. Fe oxides, % Fe_2O_3	0.014 - 0.240
Free Fe oxides, % Fe_2O_3	0.007 - 0.202
Texture	sandy loam - loamy sand

strength similar to a typical soil solution. The concentration of "water-soluble" Pb was appreciable in the surface samples (up to $20 \text{ mg} \cdot \text{kg}^{-1}$) and at the top of the groundwater table for the A and C cores (Figure 10). The concentration of water-soluble Pb was higher in the A cores, probably due to the lower pH of these samples. The concentration of soluble Pb in the background samples was often below detection limits.

For the 0.1M HCl extraction, Pb ranged up to $1100 \text{ mg} \cdot \text{kg}^{-1}$ at the surface (Figure 11). A concentration peak in dilute acid-extractable Pb was found at the groundwater table in cores A and C.

Total Pb ranged up to $21,000 \text{ mg} \cdot \text{kg}^{-1}$ (Figures 12-15). The A cores, located at the edge of the battery case pile, contained the greatest amount of Pb, although several hundred $\text{mg Pb} \cdot \text{kg}^{-1}$ were also present near the surface of Cores B and C. There was an increase in the Pb content at the groundwater table for the A and C cores (Figures 12 and 14). This appeared to correspond with an increase in pH and Mn oxide content.

It should be noted that the background sample showed an increase in total Pb content at the 1.8 m-depth and at the surface (Figure 15). This was a distance of about 300 m from the battery piles. The elevated level of Pb at the surface was probably due to automobile emissions from the nearby road (about 3 m). The increase in Pb at the 1.8 m-depth could possibly be due to migration of Pb from the surface, but this is not likely due to the high pH ($> \text{pH } 6$) below 1.2 m. It is possible, therefore, that the Pb has migrated from the contaminated area through shallow groundwater flow.

Results from the sequential extraction scheme for one core of each pair of cores will be presented for illustration. Examining the results for Core A1 (Figure 16), it can be seen that the $\text{BaCl}_2 + \text{EDTA}$ fractions and

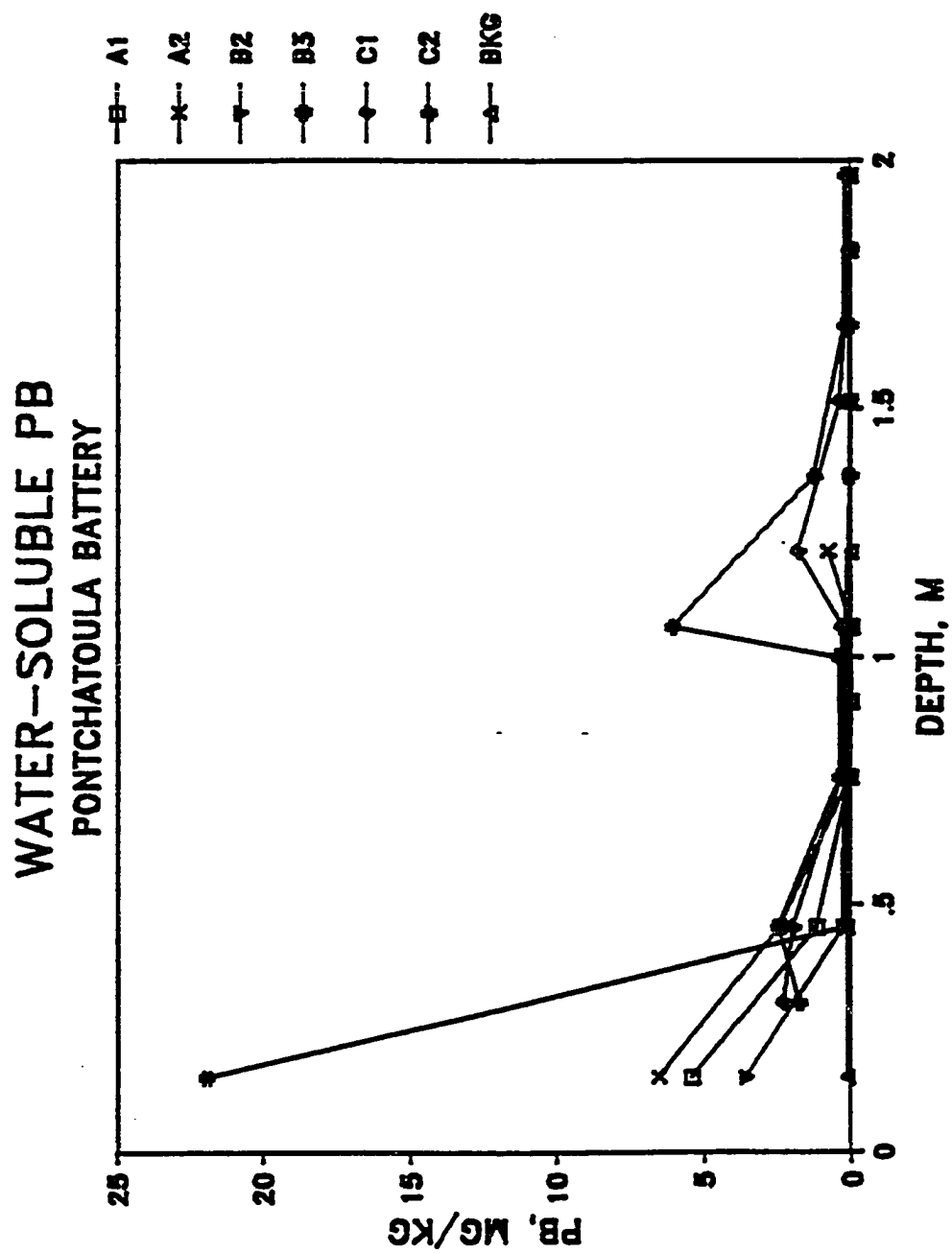


Figure 10. Water-soluble Pb with depth at Pontchatoula Battery.

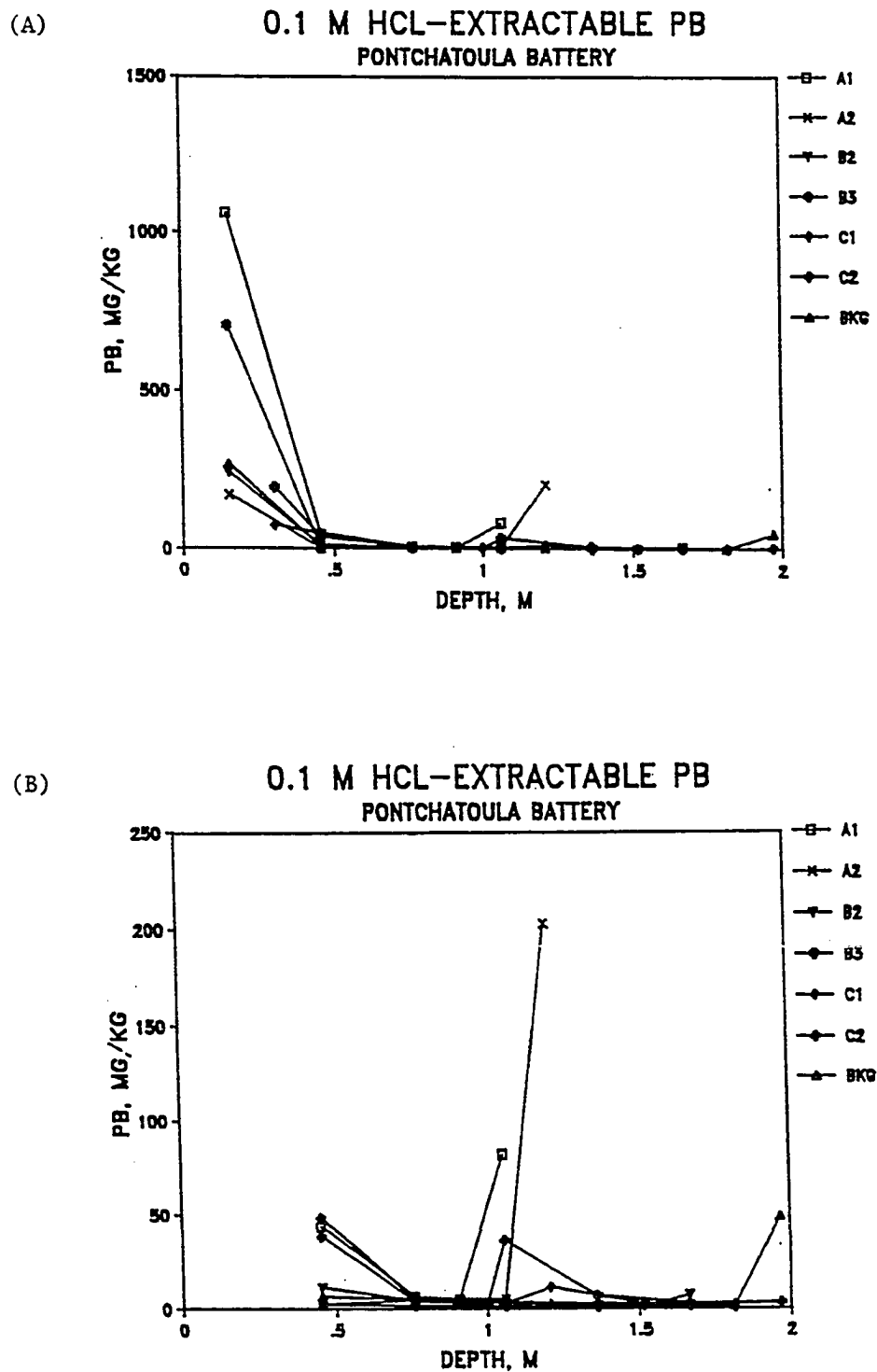


Figure 11. HCl-extractable Pb with depth at Pontchatoula Battery.

(A) Whole soil

(B) Surface horizon omitted

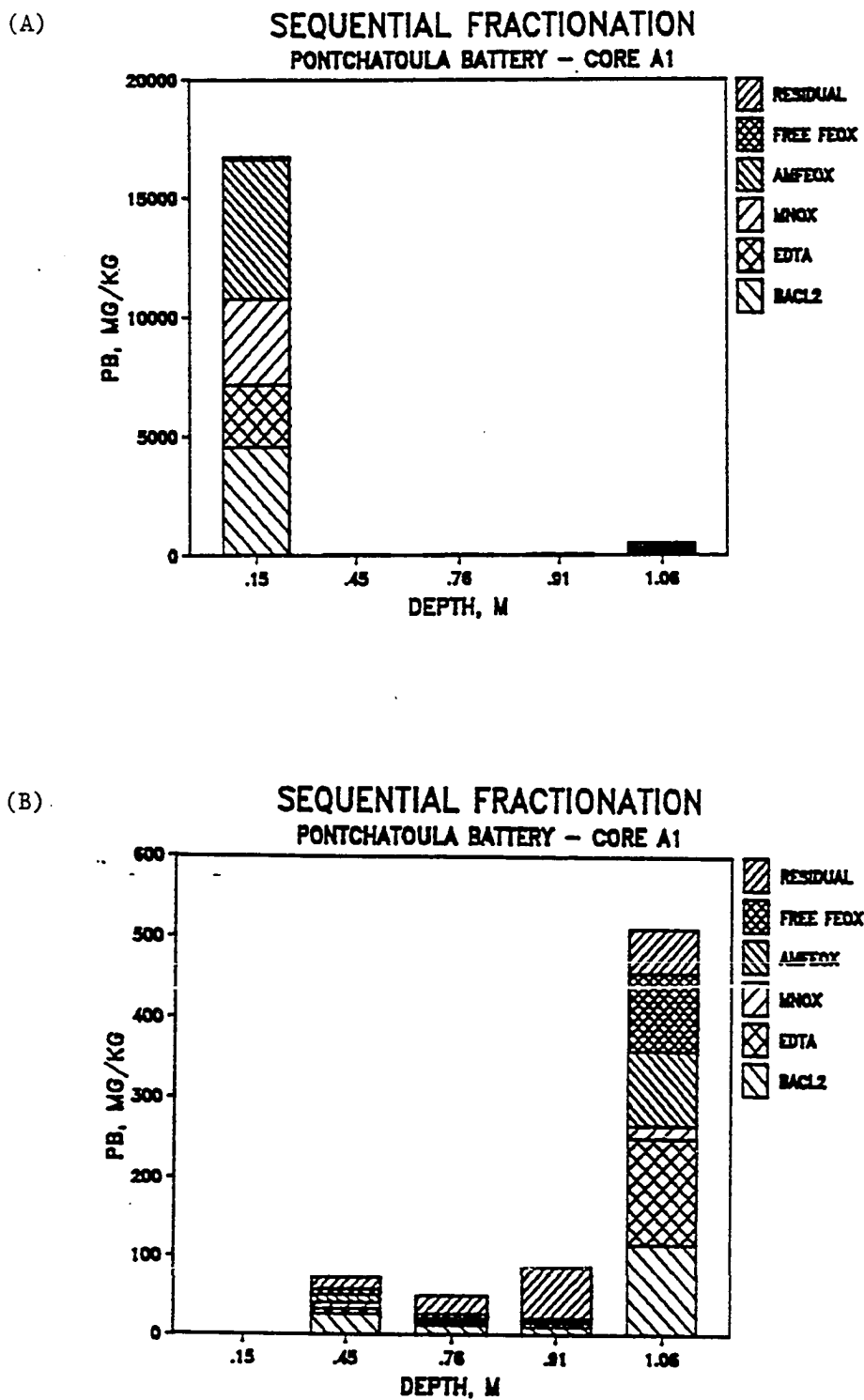
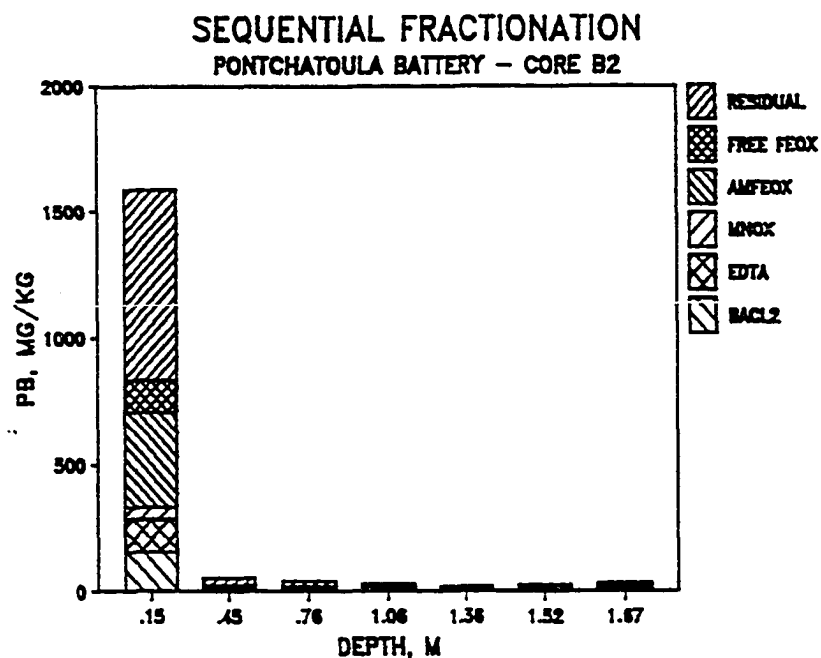


Figure 12. Lead concentrations with depth in selected chemical forms in Core A1 at Pontchatoula Battery.

(A) Whole soil

(B) Surface horizon omitted

(A)



(B)

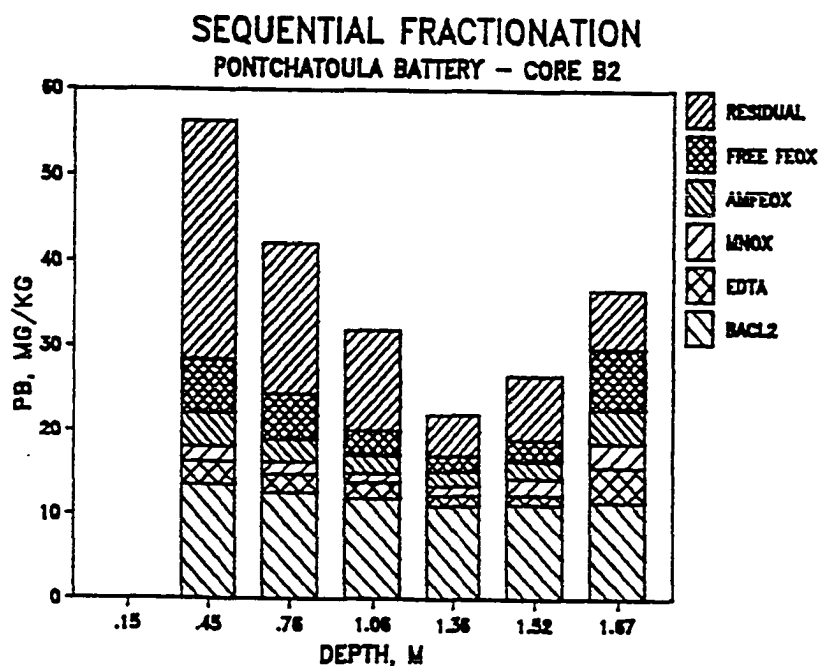


Figure 13. Lead concentrations with depth in selected chemical forms in Core B2 at Pontchatoula Battery.

(A) Whole soil

(B) Surface horizon omitted

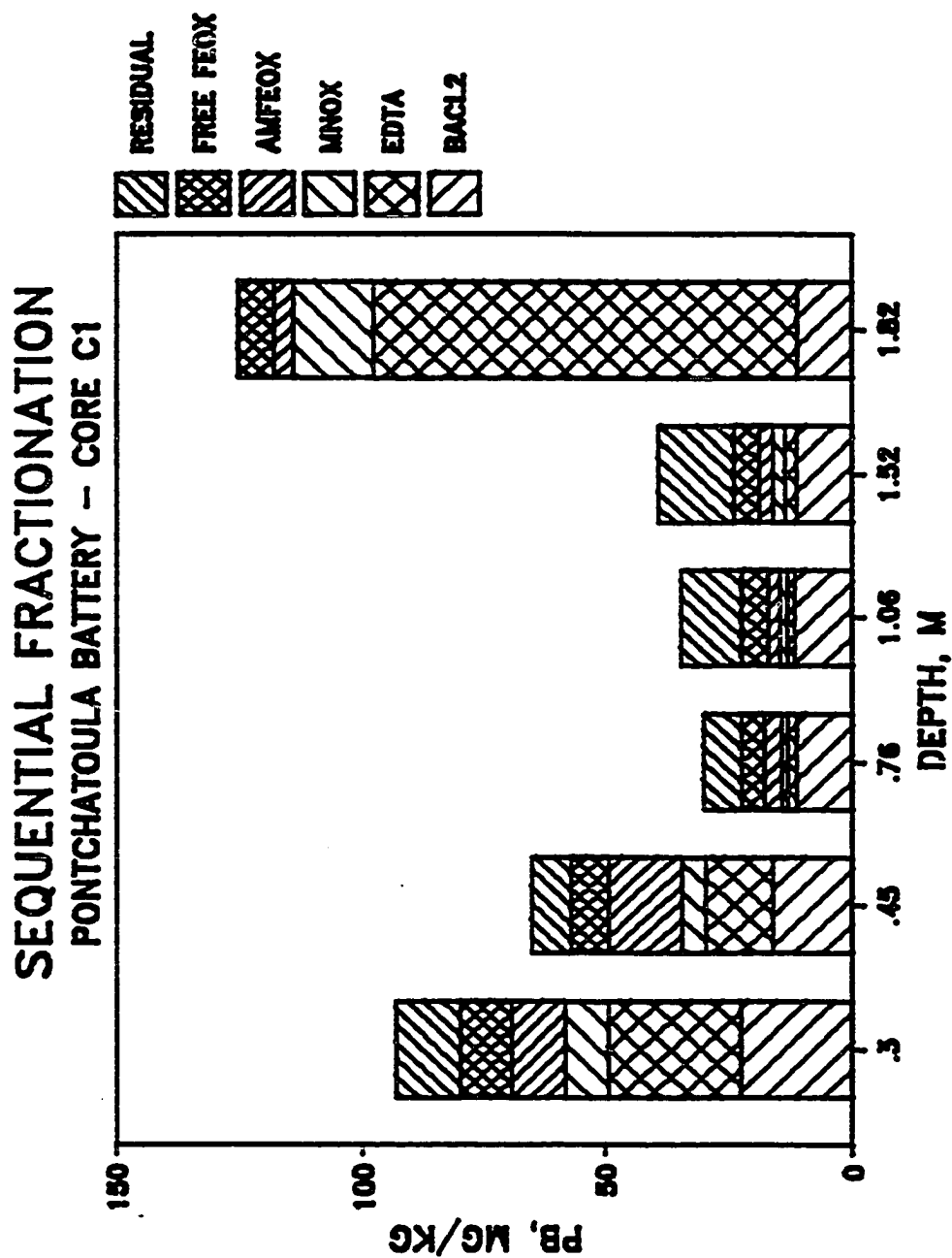


Figure 14. Lead concentrations with depth in selected chemical forms in Core C1 at Pontchatoula Battery.

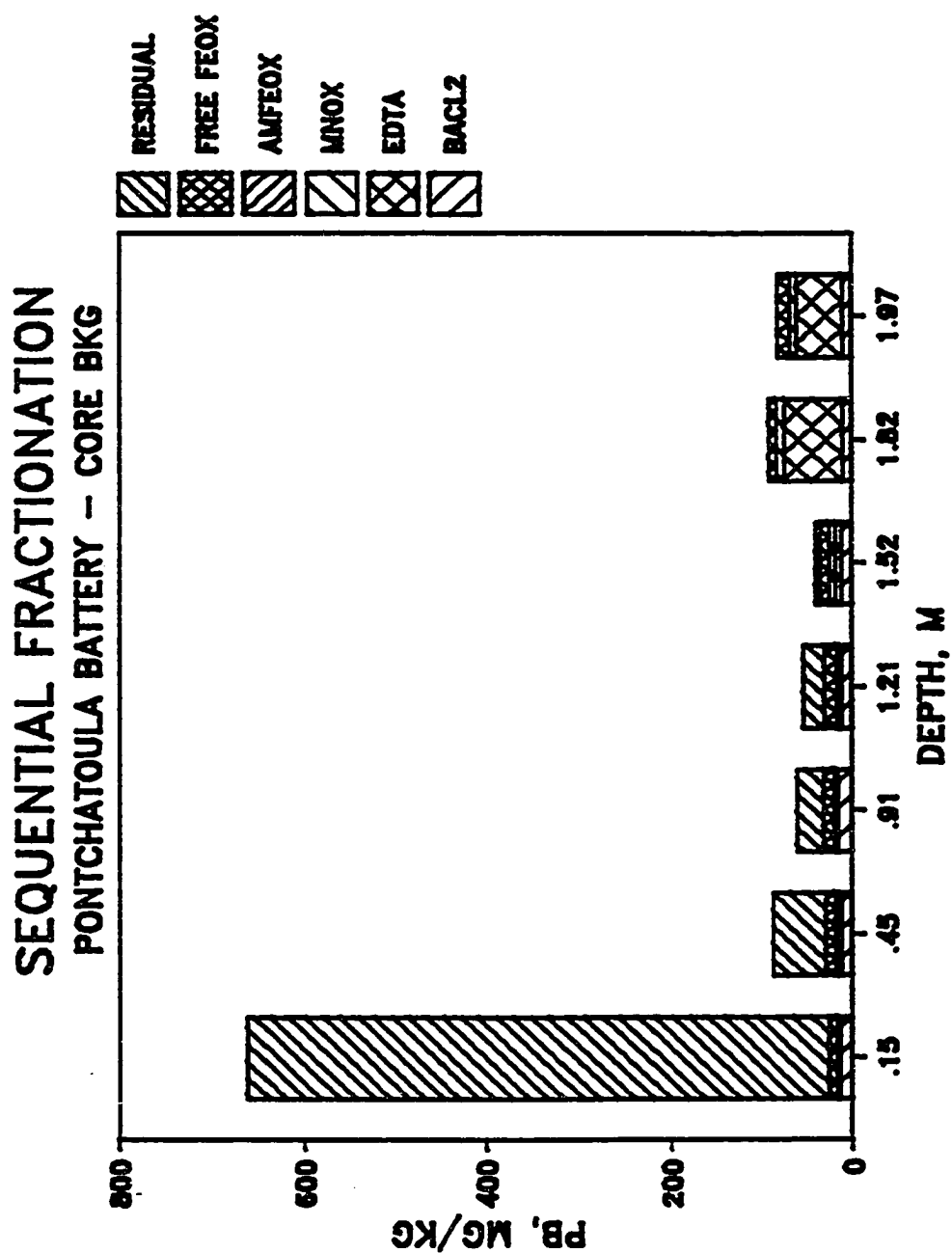


Figure 15. Lead concentrations with depth in selected chemical forms in the background core at Pontchatoula Battery.

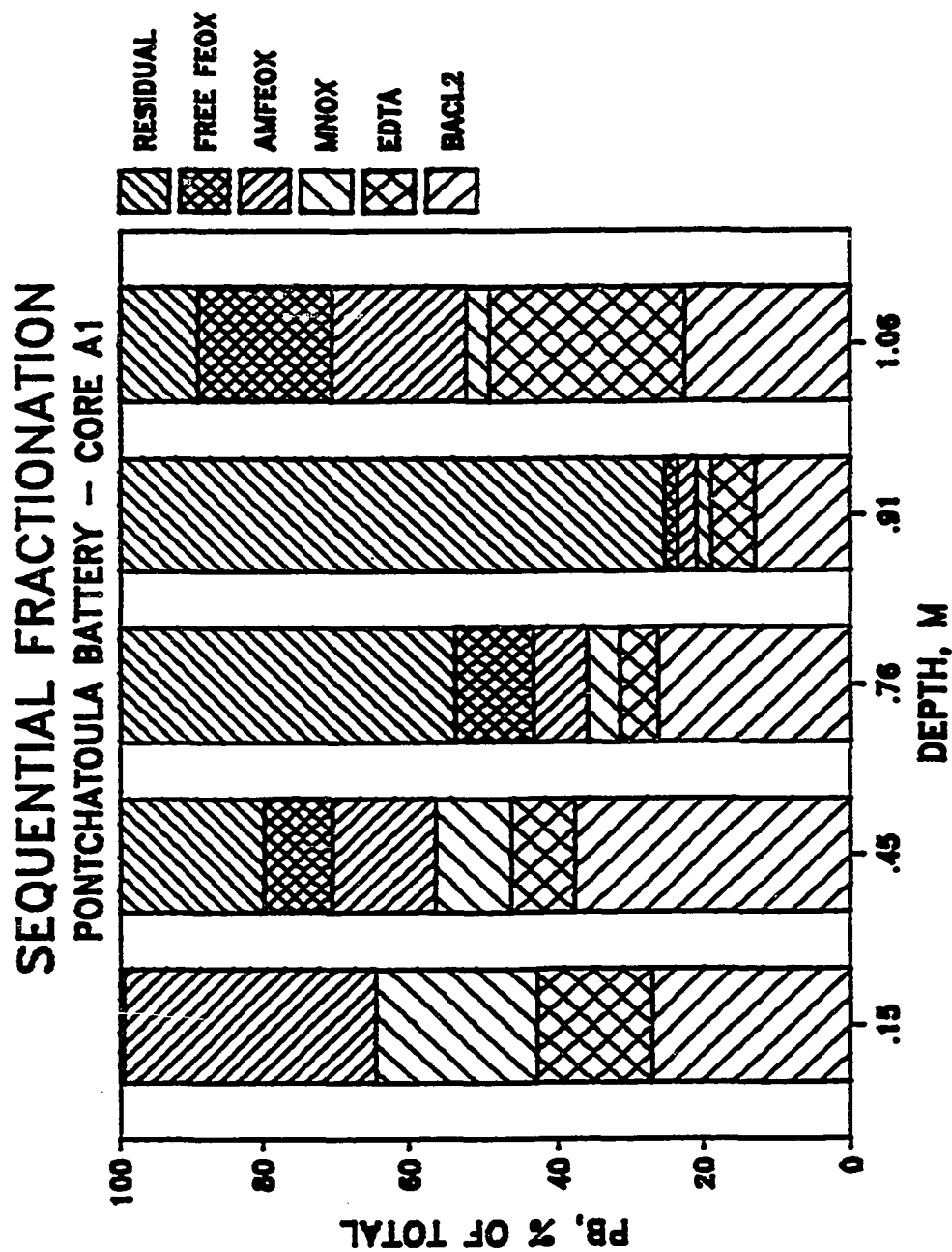


Figure 16. Distribution of Pb with depth between chemical forms in Core A1 at Pontchatoula Battery.

the amorphous Fe oxide fraction tended to decrease with depth until the sand lens (1.06 m) where they increased. The Mn oxide fraction decreased with depth. The residual fraction increased with depth until the sand lens where it decreased. Therefore, it appears that Pb availability decreased with depth until the sand lens was encountered at which point there was a marked increase in potentially available Pb. Approximately 20%-50% of the Pb was "available" (BaCl_2 + EDTA fractions) which represents a substantial amount considering the contamination levels.

For core B2, the BaCl_2 + EDTA fractions increased with depth to 1.36 m, then decreased (Figure 17). Approximately 30%-50% of the Pb was "available." The EDTA fraction was greatest at the surface and at 1.67 m. The Mn oxide fraction increased with depth below 1.06 m. The amorphous Fe oxide fraction was greatest at the surface and the 1.67 m-depth. Overall, the free Fe oxide fraction increased with depth.

For Core C1, the Pb was most available at the top of the groundwater table (Figure 18), as was seen in Core A. The total Pb was also greatest at the top of the groundwater table. Greater than 35% of the Pb in the profile was "available" (BaCl_2 + EDTA). The oxide fractions accounted for at least 20% of the Pb retained. Less Pb resided in the residual fraction than for the other cores.

The relatively available forms of Pb (BaCl_2 + EDTA) increased with depth in the background (Bkg) core (Figure 19). The Pb was very available ($> 75\%$ BaCl_2 + EDTA) at the two deepest depths (1.82 m and 1.97 m), corresponding to an increase in total Pb in the profile. Of the oxide fractions, it appears that the free Fe oxide fraction was the most important in Pb retention. The residual fraction was very important at the surface. There was more organic matter at the surface of the bkg core

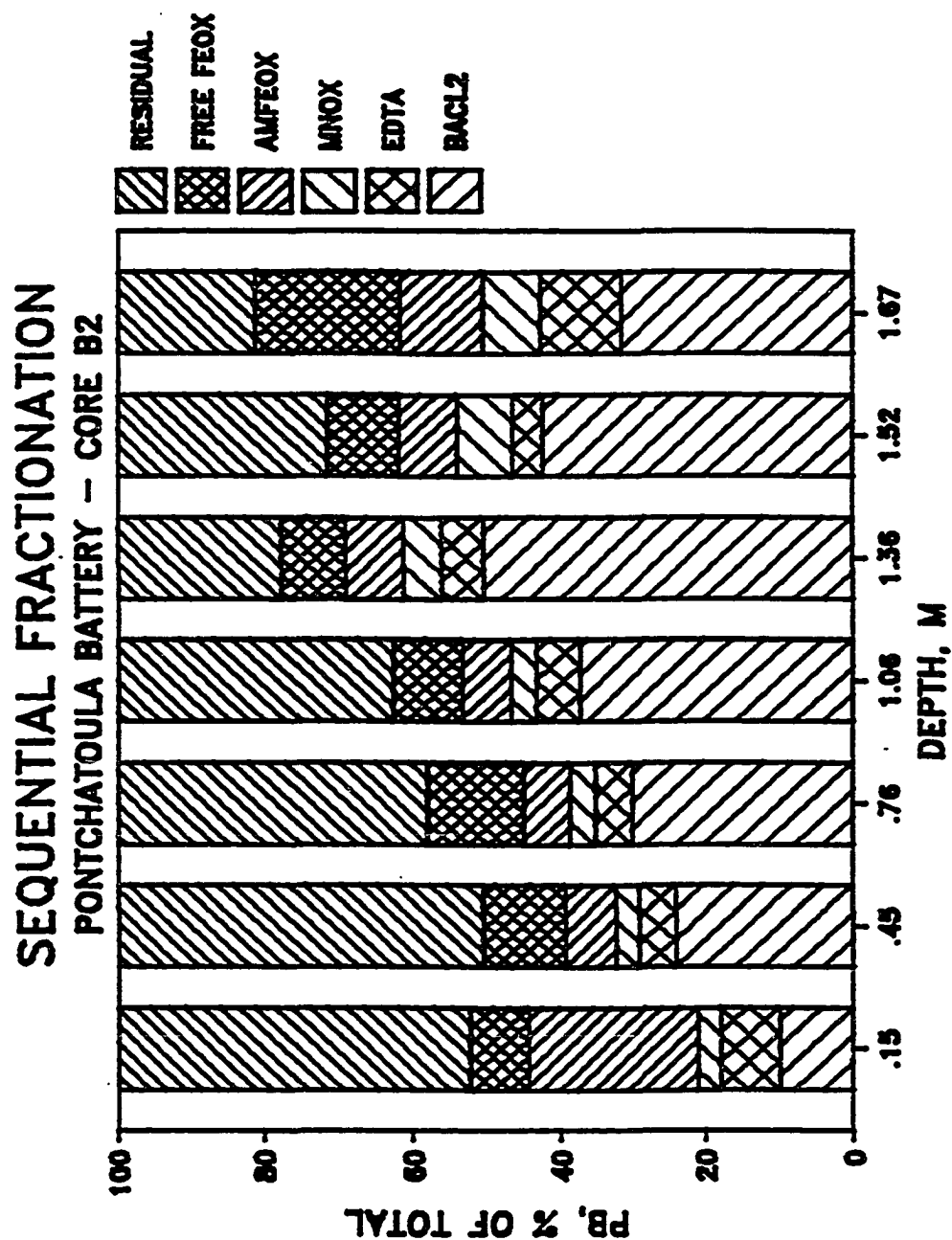


Figure 17. Distribution of Pb with depth between chemical forms in Core B2 at Pontchatoula Battery.

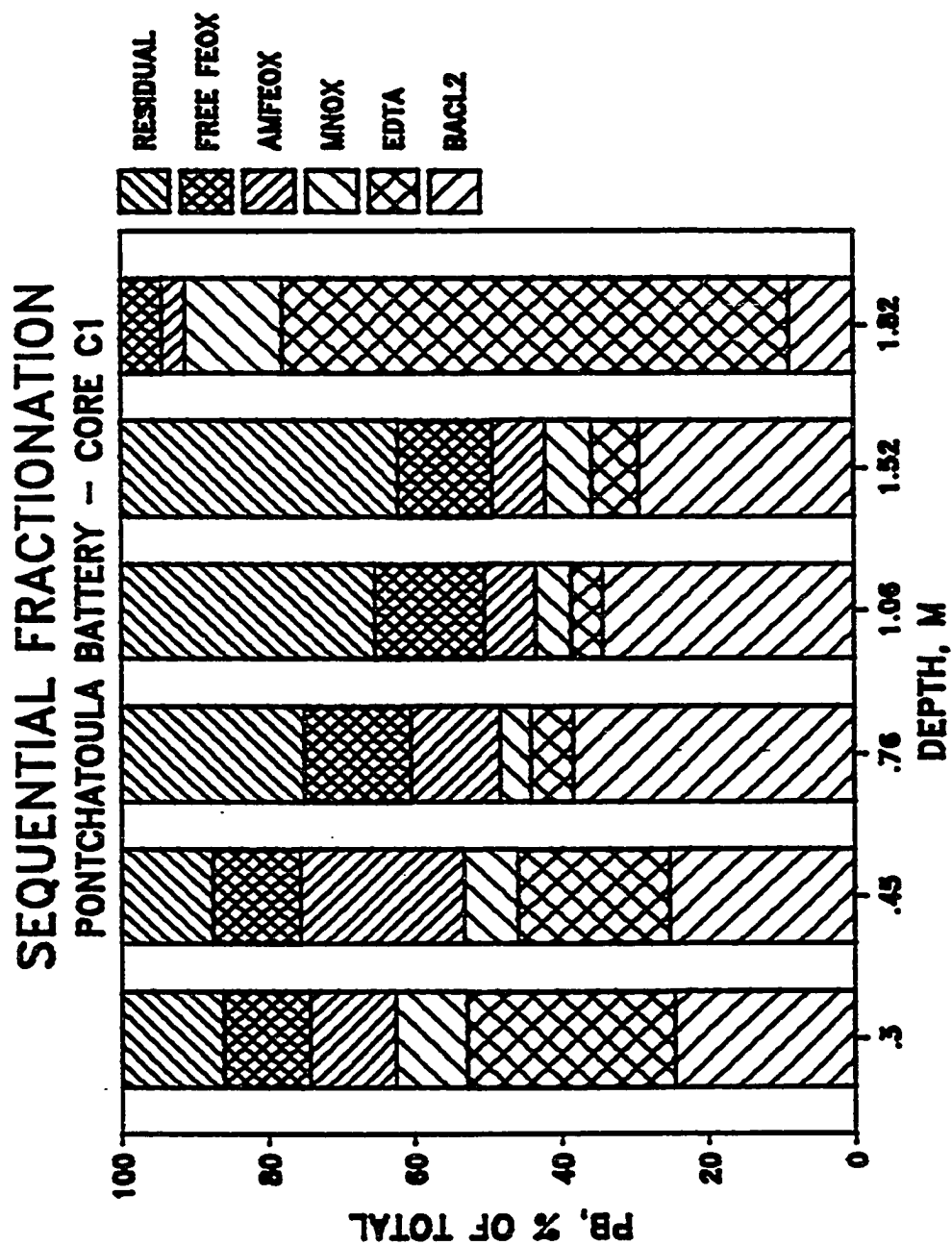


Figure 18. Distribution of Pb with depth between chemical forms in Core C1 at Pontchatoula Battery.

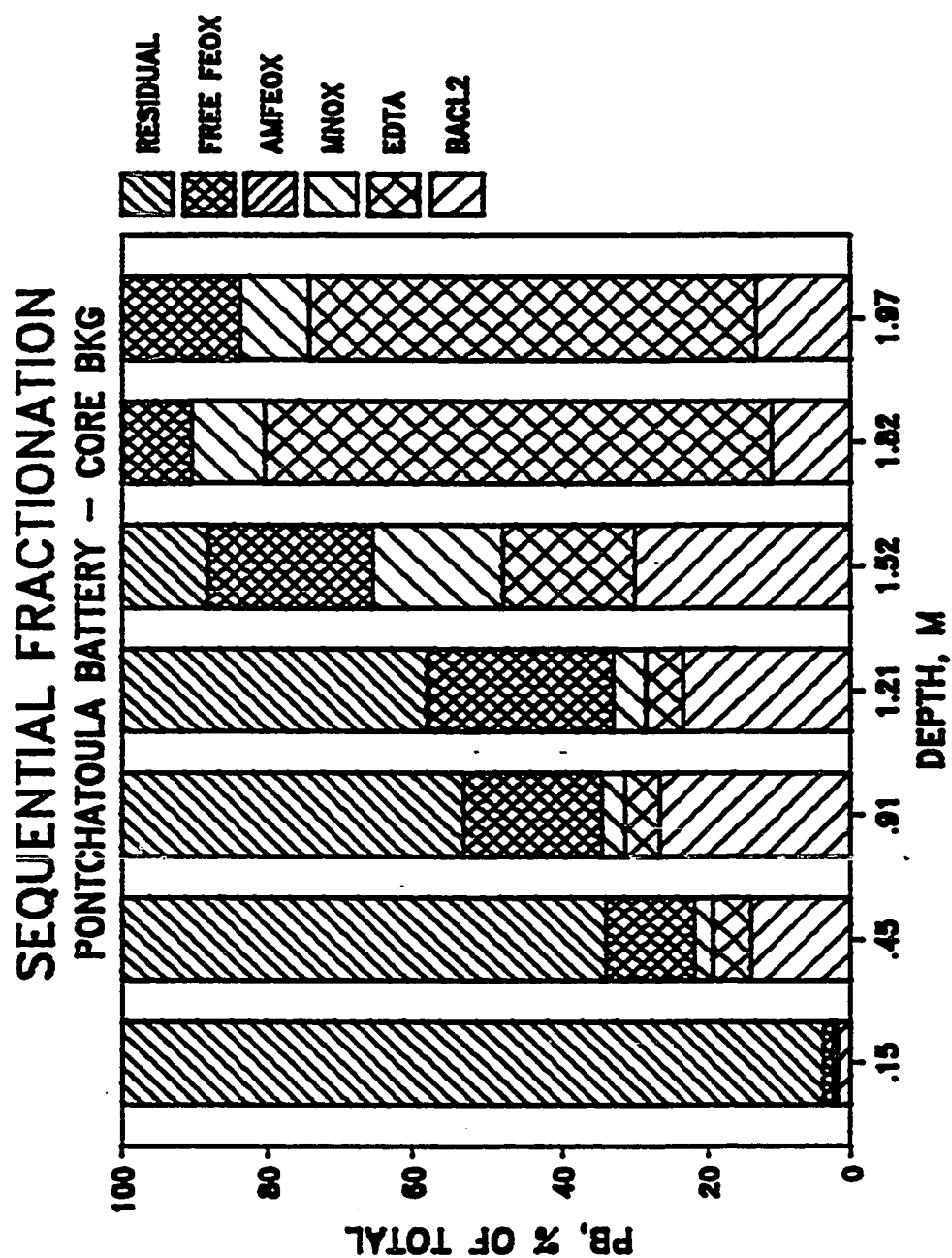


Figure 19. Distribution of Pb with depth between chemical forms in the background core at Pontchatoula Battery.

than the contaminated cores, and this large residual fraction may include Pb bound to soil organic matter.

Long-Term Release of Pb

Lead was released from the soils over time (Figure 20), especially from the A2 core (PA2-1 A and B). Up to $150 \text{ mg Pb} \cdot \text{L}^{-1}$ was released from the A2-1 samples. This was approximately a seven-fold increase in Pb in solution over the two month period. Release of Pb from the other samples was not as great. Levels of exchangeable Pb in the A2-1 soil sample were much greater than in the other samples. Therefore, release from the A2-1 samples was greater than from the other samples. For the A2-5 and B2-7 samples, Pb was readsorbed during the first O_2 cycle, then released over the remaining time. The release of Pb did not seem to be affected by the purging gas.

Iron (Figure 21), and to a much lesser extent Mn (Figure 22), was released over time, particularly during Ar purging, possibly due to reduction of Fe(III) and Mn(IV) to Fe(II) and Mn(II) and subsequent release to solution. This was supported by the decrease in the redox potentials of the samples with time (Figure 23), although the measured values indicated that the Eh was not low enough to reduce Fe(III) and Mn(IV).

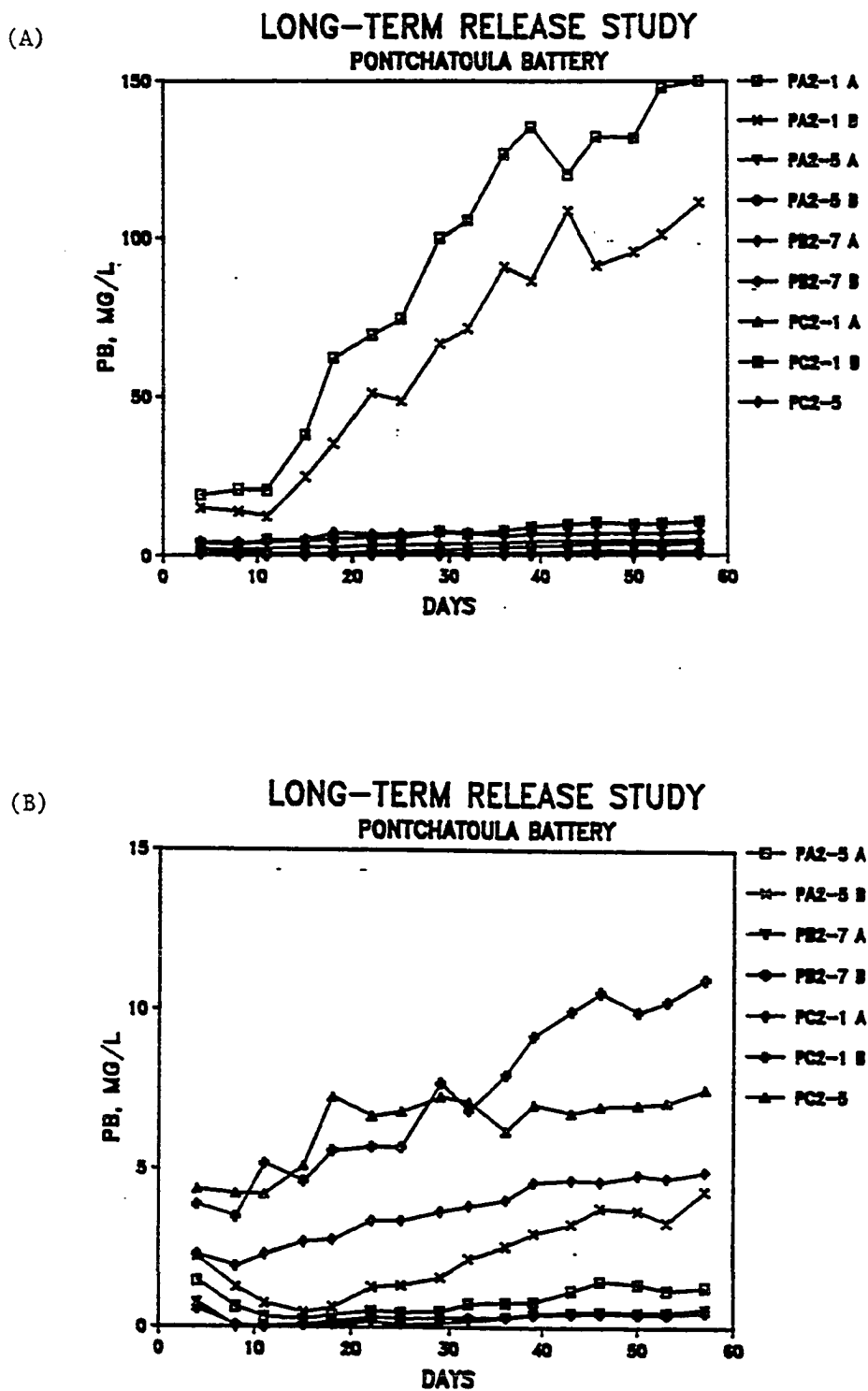


Figure 20. Release of Pb over time from selected contaminated soil samples from Pontchatoula Battery.

(A) All samples

(B) PA2-1 samples omitted

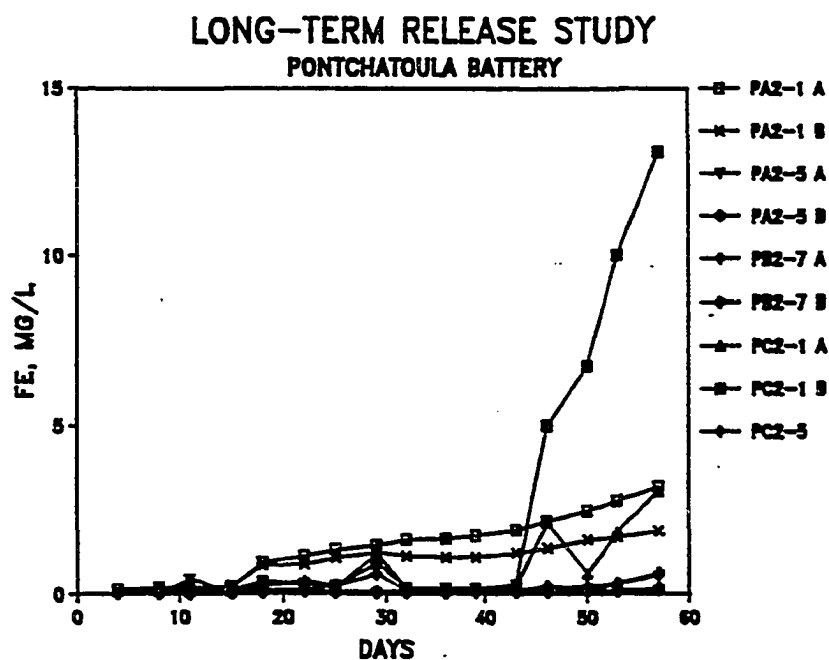


Figure 21. Release of Fe over time from selected contaminated soil samples from Pontchatoula Battery.

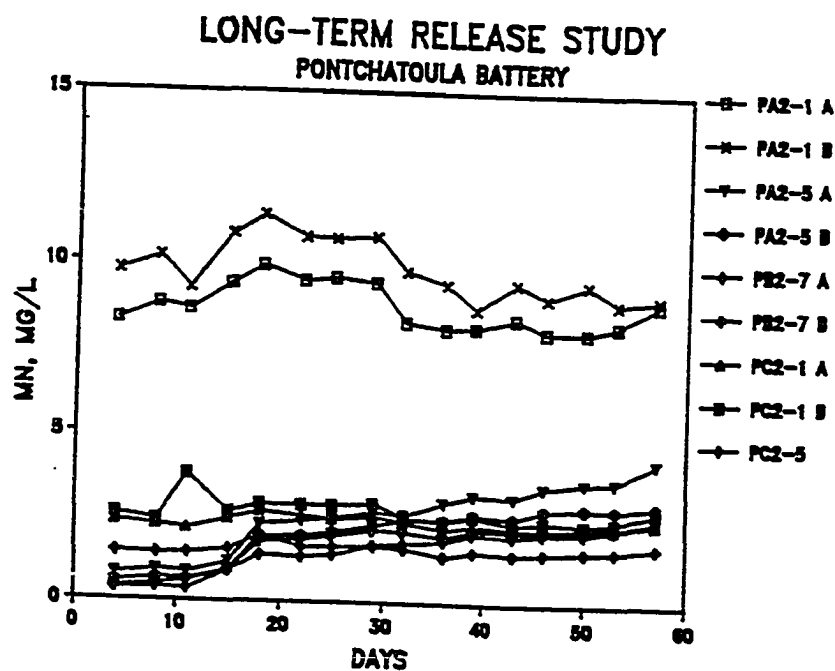


Figure 22. Release of Mn over time from selected contaminated soil samples from Pontchatoula Battery.

LONG-TERM RELEASE STUDY PONTCHATOU LA BATTERY

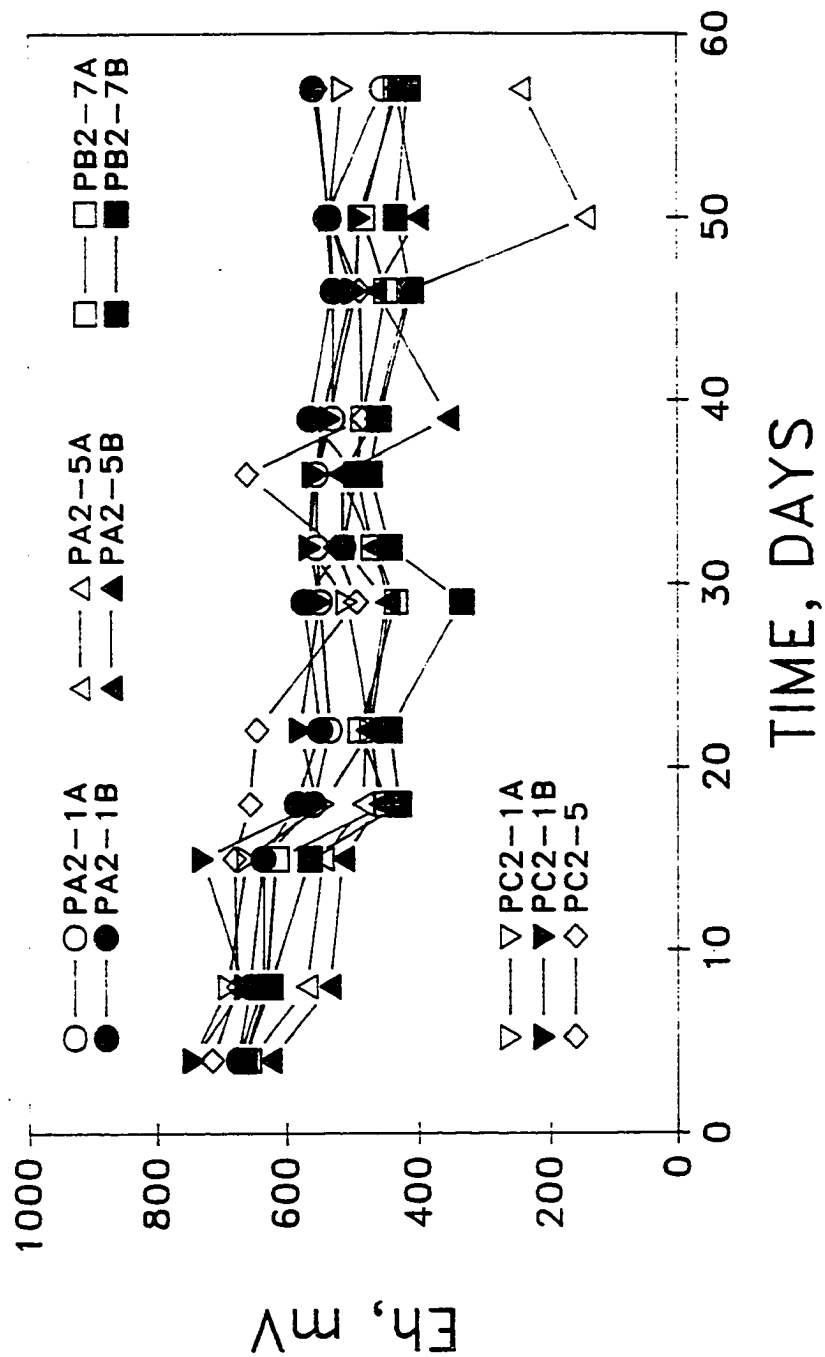


Figure 23. Redox potential versus time during long-term release study.

DISCUSSION

Chemical Forms

The greatest concentration of Pb was typically found at the soil surface. This very high concentration of Pb was due to direct deposition of Pb from the battery cases. At the Sapp Battery Site in Jackson County, Florida, the maximum concentration of Pb was found in the upper 0.67 m - 1 m of soils (Watts, 1984). As at Pontchatoula Battery, the battery cases were not cleaned prior to disposal.

The concentration of Pb decreased with depth in cores A and C, then increased at the top of the groundwater table. This increase appeared to correspond with an increase in pH and Mn oxide content. The pH in and near the groundwater table was higher than at shallower depths probably because of the dilution effect of groundwater moving laterally under the leaching acid. The higher pH and Mn oxide levels likely contributed to precipitation and adsorption processes immobilizing some of the Pb in this zone that moved from higher, more acid parts of the profile. Lead solubility has been found to decrease as pH increased (Santillan-Medrano and Jurinak, 1975). Also, the retention of Pb by hydrous Mn oxides has been reported to increase linearly with pH in the range pH 2 to pH 6 (Gadde and Laitinen, 1974).

Comparing the sequential fractionation results across the cores, it appears that much of the Pb is found in relatively available forms. Gambrell et al. (1976, 1980), in a study on redox effects on Pb availability, concluded that most of the labelled Pb and approximately half of the total indigenous Pb in a coastal sediment were recovered in potentially available forms, but usually less than 5% in the most readily

available forms. Gerritse and van Driel (1984) calculated that the exchangeable fraction of Pb in samples studied was in the range of 1% - 5% also. Like the sediment Gambrell et al. studied, these soils were surface soils which had a higher pH and organic matter content than the soil at the Pontchatoula site, probably accounting for the differences in the results.

Much of the increase in retained Pb at the top of the groundwater table was in the exchangeable phase. This lack of more effective immobilizing processes in the deeper sandy soil is important in terms of the potential for mobility. That is, much of the retained Pb at the top of the groundwater table is relatively weakly retained in a form that can easily be displaced, favoring its movement through the lower subsoil or laterally through the soil. The amount of Pb in the more readily available fractions often was greater than the amount of Pb in the oxide fractions. Thus, the elevated Pb at 1.8 m in the profile expected to be a control site likely was the result of lateral transport several hundred meters from the spill site.

The oxide fractions have been shown to be an important process in regulating Pb availability. Lion et al. (1982) reported that 70% of the extractable Pb in sediment samples from South San Francisco Bay estuary was associated with the Fe and Mn oxides. However, in this relatively coarse textured, acid soil with low levels of hydrous metal oxides and high levels of waste Pb, it is apparent that the oxide fractions cannot and have not effectively immobilized Pb. This is supported by the elevated Pb levels in deeper sections of the control core and the long-term release study.

It should be noted that there appeared to be a significant depth by extractant interaction indicating that the order of extractability of the Pb in the different chemical forms varied with depth. This was noted in the above comparison of the extractions in the different cores. The extractable Pb was greatest in the surface sample followed by the sample at the top of the groundwater table.

Correlation Between Extractable Pb and Soil Properties

Simple correlation coefficients were determined for the associations between extractable Pb and selected soil properties for the whole soil (Table 4). The statistically significant, but weak, negative correlation between H₂O-soluble Pb and soil pH was due to the fact that the very high levels of Pb were in the acidic surface horizon and the strongly acid conditions kept some of the Pb in readily mobile forms.

Examining just the surface horizon, total Pb was correlated with Mn oxide content, but again, this was a very weak correlation (Table 5). Looking at the sand lens where a peak in Pb concentration was observed, extractable and total Pb were correlated with Mn oxide content (Table 6). This correlation to Mn oxide content may be a direct result of increased pH leading to coprecipitation of Pb with Mn oxide (Hem, 1978, 1980). The retention of Pb by hydrous Mn oxide was reported to increase linearly in the pH range pH 2 to pH 6 (Gadde and Laitinen, 1974). As was noted earlier, it has been reported that Pb solubility decreased as pH increased (Santillan-Medrano and Jurinak, 1975).

The Pb retention mechanism at Sapp Battery was not related to CEC or clay content (Watts, 1984). It was concluded that the Pb levels were probably due to deposition of Pb oxide suspended in acid plus mixing to

Table 4. Simple correlation coefficients relating extractable Pb to soil properties - Whole soil.

Fraction	Soil pH
<hr/>	
H ₂ O-soluble	-0.324*

All other fractions were not significantly related to pH

not significant: extractable Pb with Mn oxides, Fe oxides, CEC, or particle-size.

* significant at 0.05 level.

Table 5. Simple correlation coefficients relating extractable Pb to soil properties - Surface horizon only.

Fraction	Mn oxides
<hr/>	
Total Pb	0.864*

All other fractions were not significantly related to Mn oxides

not significant: extractable Pb with pH, Fe oxides, CEC, or particle-size.

* significant at 0.05 level

Table 6. Simple correlation coefficients relating extractable Pb to soil properties - Sand lens only.

Fraction	Mn oxides
<hr/>	
BaCl ₂ -extract. Pb	0.889*
EDTA-extract. Pb	0.926**
Pb assoc. with Mn oxides	0.990**
Pb assoc. with Amorph. Fe oxides	0.887*
Residual Pb	0.830*
Total Pb	0.992**

not significant: extractable Pb with pH, Fe oxides, CEC, or particle-size.

*, ** significant at 0.05 and 0.01 level, respectively.

a 1 m-depth with a front-end loader and to subsequent infiltration followed by precipitation or exchange. Precipitation, adsorption, cation exchange, etc., appeared to play a minor role to deposition where excess Pb was found (Watts, 1984). At Pontchatoula Battery, however, the lack of sufficient retention capacity resulted in Pb movement to shallow groundwater.

Long-Term Release of Pb

The release of Pb was weakly related to the release of Fe and Mn. This indicates that some Pb was retained (adsorbed and/or occluded) by Mn and Fe oxides, which upon being reduced, released Pb.

The release of Fe and Mn (and Pb) was least under the first air cycle than throughout the rest of the experiment. Iron and Mn were still released under the second air cycle for most samples. Thus, oxidizing conditions were apparently not re-established during the two-week air cycle. The redox potentials of the samples did not increase during the second air cycle (Figure 21). Also, Khalid et al. (1978) reported that Pb may be released under slightly acidic, oxidizing conditions due to H^+ displacement.

The results of the long-term release study were consistent with the results from the extraction work. Lead was released from the surface samples and would be available to migrate down the soil profile, corresponding to what was observed at the site. The release of Pb coincided to some extent with release of Fe and Mn indicating that some Pb was retained by the hydrous metals oxides. However, as noted earlier, the measured Eh values indicated that the Eh of the soil suspension was not low enough for Fe and Mn oxide dissolution. The interaction of pH

with Eh was not taken into account to determine this; thus, since the pH of the suspension was acidic, Eh may have been low enough for oxide dissolution. It is possible that since the system was not well poised, the measured values are inaccurate, and should be used only as a guide to the redox status of the soil suspension. It is also possible that other mechanism may have been involve in Fe and Mn release. Sequential extractions on the samples from the site and correlation relationships also showed the importance of the oxides, particularly Mn oxide, in retaining Pb.

SUMMARY AND CONCLUSIONS

Higher concentrations of Pb were found at the soil surface and the top of the groundwater table than in the intermediate zone. The higher concentrations of Pb at the groundwater table were associated with higher pH levels and higher Mn oxide levels. The percentages of Pb extracted with the different extractants varied with depth suggesting possible changes in the form of Pb with depth. Water-soluble Pb was negatively correlated with pH. Several extractable forms of Pb were correlated with Mn oxide at depth. This may be due to coprecipitation of Pb and Mn at the higher pH level measured at the groundwater table. Long-term release studies showed that Pb could be mobilized in this soil and supported the soil extraction and site characterization results. At this site, Pb movement to shallow groundwater has been facilitated by the presence of strong acid. There is some evidence that Pb may be moving off the site in groundwater flow.

The water analysis, soil extraction, and long-term release results all indicated that the initial forms of Pb deposited at the site are unstable in the soil environment found at the site, thus making the Pb somewhat mobile, that significant movement of Pb has occurred, and that, although some association of Pb with metal oxides was found, existing chemical conditions and the lack of large quantities of metal oxides in the soil at the site do not favor effective immobilization of Pb.

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CHAPTER 3

THE DISTRIBUTION AND ENVIRONMENTAL CHEMISTRY OF ARSENIC
IN SOIL AT AN ABANDONED ARSENIC DIPPING VAT

ABSTRACT

The distribution and environmental chemistry of As in soil was determined at an abandoned As dipping vat near Kolin, Louisiana. Higher As concentrations were found at the soil surface and at shallow depths. Sequential selective extractions showed that the chemical forms of As varied with depth. Significant correlations between As and pH, CEC, and metal oxides were observed. In particular, Fe oxides were indicated to effectively immobilize As in the near-surface soil. Less total As and Fe oxides were found deeper in the profile, but more of the As at these depths was in potentially mobile forms. Long-term laboratory release studies showed only a slight increase in soluble As over time, indicating low mobility of As, as was seen at the site.

INTRODUCTION

Potential for arsenic (As) contamination of groundwater in Louisiana exists due to abandoned As dipping vats. The vats were used during the 1920s to 1950s to remove parasites, particularly the tick which caused

Texas cattle fever, from cattle and horses. Spillage from the vats has contaminated adjacent soil and may have migrated to the groundwater.

The distribution and migration potential of As in soils contaminated with As-containing wastes is dependent upon the physical and chemical properties of the soils and the waste's characteristics. Some of the factors affecting As movement include speciation of As, redox potential, pH, type and amount of clay minerals, and metal oxides content.

Arsenic can exist in four valence states (-3, 0, +3, +5) depending on pH, redox potential, and other factors, as well as inorganic and organic complexes. Transformations from one As species or oxidation state to another result from chemical or biological reactions. The inorganic chemical reactions are a function of pH and Eh (Holm et al., 1979).

Arsenic retention is predominately by the poorly crystalline hydroxy-Fe and hydroxy-Al compounds of recent weathering (Livesey and Huang, 1981). Ferric oxide retained As(III) while Fe(III) oxide and n oxide retained little As(V) (Oscarson et al., 1981). Fuller (1978) reported that As retention could be predicted at the 95% confidence level by an equation including percent clay, surface area, and percent Fe oxides as the independent variables.

The objectives of this study were: (1) to determine the distribution of As in soil cores at an abandoned As dipping vat; (2) to determine the quantities of As associated with specific mineral phases using a sequential extraction scheme; (3) to relate As distribution to soil properties; and (4) to determine long-term release from As-contaminated soil under alternating oxidizing/reducing conditions.

MATERIALS AND METHODS

Site Description

Arsenic dipping vats were used during the 1920s to 1950s to remove parasites from cattle and horses. The vats were narrow and long and constructed of concrete-lined pits dug into the ground. The cattle and horses were led to the entrance apron and forced to jump into the vat, which was approximately 2 m deep. The animals then swam the length of the vat and walked up the ascending floor to exit the vat.

The vat in this study was located near Kolin, La., along La 107, approximately 0.7 km west of the junction with La 454. The vat was approximately 1 m across and approximately 10 m long.

The soil in the vicinity of the pit was of the Acadia-Kolin association (fine, montmorillonitic, thermic, Aeric Ochraqualfs). This association consists of loamy upland soils that have a clayey subsoil. Slopes are 0.5 to 5 percent.

Preliminary results of soil cores taken by the Louisiana Department of Transportation and Development (LA. DOTD) indicated high levels of total As in the soil (up to $1000 \text{ mg} \cdot \text{kg}^{-1}$) to depths of 2 m.

Sampling Procedures

Soil cores were obtained using commercial equipment that hydraulically presses a stainless steel core extractor tube (4.75 cm diameter) into the ground. Duplicate core samples were taken at three locations surrounding the vat, as indicated in Figure 1. The first pair of cores, A1 and A2, were obtained from the north (road) side of the vat approximately 1.5 m east of the entrance apron. Cores B2 and B3 were also

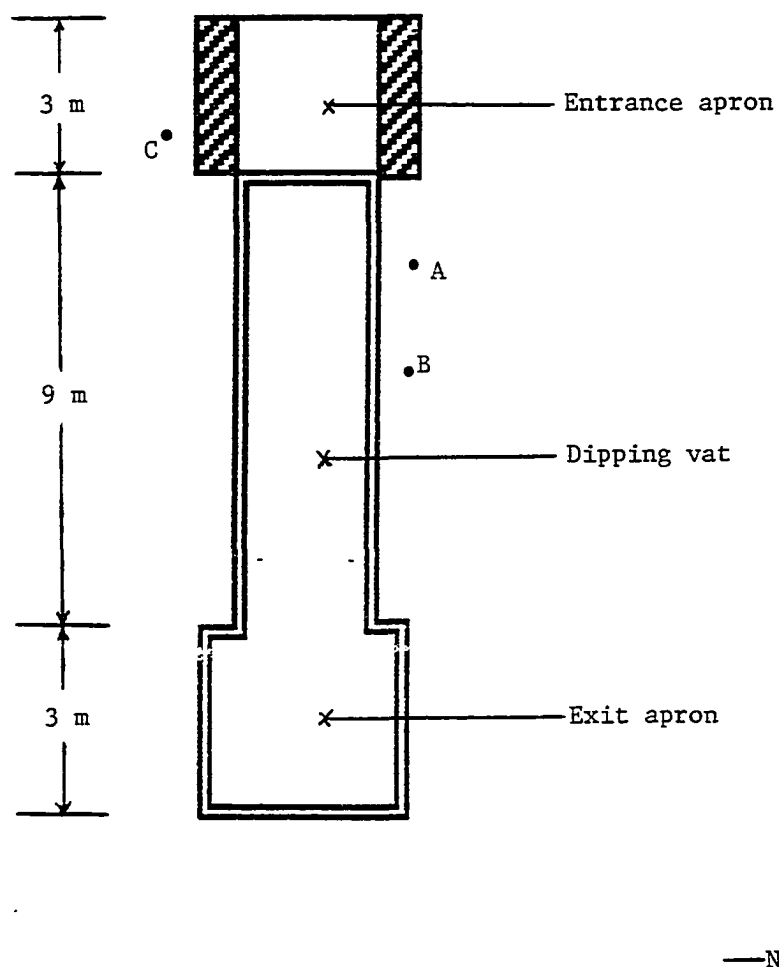


Figure 1. Location of cores sampled at Kolin As dipping vat, Kolin, Louisiana.

taken on the north side of the vat approximately 3.5 m east of the entrance apron. Cores C2 and C3 were obtained on the south side of the vat next to the entrance apron. Background samples were obtained from a site across the road from the vat.

After the cores were pulled to the surface, they were sectioned by depth and/or horizon and placed in 1-L plastic storage bottles. The samples were refrigerated upon return to the laboratory to preserve conditions found in the field.

Groundwater samples were obtained from Core A1 using vacuum extraction. Water samples were also obtained from the vat itself. Upon return to the laboratory, the samples were filtered through a 0.45 μm membrane filter and analyzed for pH, then acidified and analyzed for elements of interest (particularly As) by ICP (inductively-coupled plasma) spectroscopy.

Soil Physical and Chemical Characteristics

Soil samples were not dried prior to analysis of soil properties to preserve field conditions. Water content was determined by the water loss on drying at 105° C (Gardner, 1986) and was used to report all extraction concentrations on a dry weight basis. The pH of the samples was determined according to the method of McLean (1982). Cation exchange capacity (CEC) was determined by summing the major cations (Ca, Mg, Na, K, and Al) extracted with 0.1M BaCl₂ (adapted from Rhoades, 1982). Particle-size distribution was determined by the hydrometer method (Gee and Bauder, 1986). The Mn oxide content of the samples was measured using pH 2, 0.1M hydroxylamine hydrochloride (Chao, 1972). Amorphous Fe oxides were determined using 0.25M hydroxylamine hydrochloride-0.25M HCl (Chao and

Zhou, 1983). Free (crystalline + amorphous) Fe oxides were determined using the dithionite-citrate-bicarbonate (DCB) method (Mehra and Jackson, 1960). Crystalline Fe oxides were determined by subtracting the amorphous Fe oxide content from the free Fe oxide content.

Chemical Forms

The soil samples were extracted to determine selected chemical forms of As in the soil using the sequential fractionation scheme outlined in Figure 2. This design is not based on any particular scheme in the literature, but is similar to several used by other investigators (Pickering, 1981; Salomons and Forstner, 1984). The scheme consists of extracting Mn oxides, amorphous Fe oxides, and free Fe oxides in sequence preceded by extractions with a neutral salt (BaCl_2) and a chelating agent (EDTA). Since As is present as an anion in soils, easily exchangeable As can be exchanged by the chloride in the BaCl_2 extractant, and As anion species associated with metal cation species sorbed to the soil can be extracted when weakly and strongly sorbed metal cations are extracted with the BaCl_2 and EDTA. The extractants in the sequential fractionation scheme were intended to extract As associated with the following chemical phases in soils: (1) BaCl_2 - weakly sorbed and exchangeable As (Cl^- replacing weakly held As anions); (2) EDTA - As associated with readily extractable Ca, Fe, etc.; (3) pH 2, 0.1M $\text{NH}_2\text{OH}\cdot\text{HCl}$ - As associated with Mn oxides (4) 0.25M $\text{NH}_2\text{OH}\cdot\text{HCl}$ -0.25M HCl - As associated with amorphous Fe oxides; and (5) DCB - As associated with free Fe oxides (crystalline Fe oxides + amorphous Fe oxides not extracted by extractant (4)). The metal oxide extractants recover sorbed As not extracted by the BaCl_2 and EDTA as well as As occluded by the metal oxides.

SEQUENTIAL FRACTIONATION SCHEME

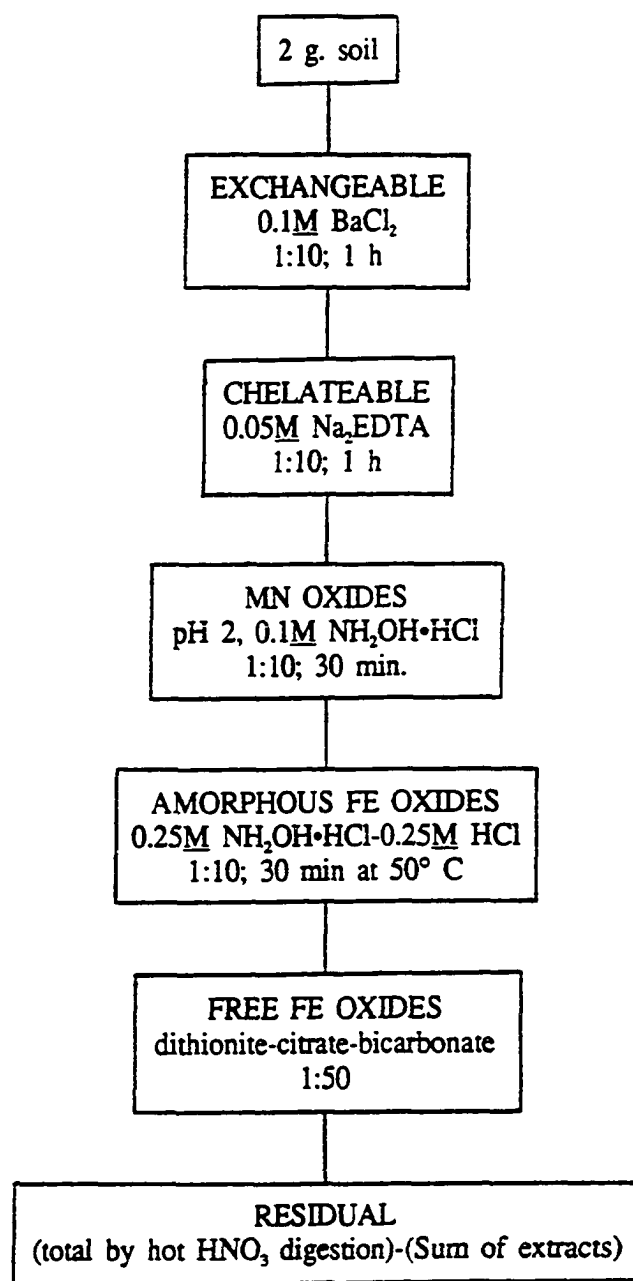


Figure 2. Sequential fractionation scheme used to determine the distribution of As in the soils at Kolin As kipping vat.

The water-soluble, acid-extractable, and total As in the soil were determined on separate aliquots of soil using the methods listed in Table 1. Separate soil aliquots were used for these extractions because: (1) water-soluble As levels were typically low, requiring a larger sample than that used in the sequential extraction scheme; (2) the 0.1N HCl does not extract a specific phase but extracts potentially available As in several phases; and (3) it may be difficult to determine the low levels of residual As in soil after the fractionation scheme. The residual fraction was determined by subtracting the sum of As extracted in the sequential fractionation from the total As determined on a separate aliquot. A dilute salt solution (0.005M $\text{Ca}(\text{NO}_3)_2$) was used in place of deionized water for the "water-soluble" phase to better mimic the soil solution and to facilitate filtration (Amacher, 1984).

Long-Term Release of As

To determine if As is being released over time and if this release is affected by changing redox conditions, 0.005M $\text{Ca}(\text{NO}_3)_2$ was added to selected contaminated soil samples from the site at a soil/solution ratio of 1:10 and continuously shaken on a reciprocating shaker at 140 $\text{osc}\cdot\text{min}^{-1}$. The soil/solution mixtures were purged daily with air (designated as O_2 in text and figures) for two weeks, then with Ar for two weeks, then again with air for two weeks, then with Ar for two weeks using the experimental setup described in Chapter 6. The suspensions were sampled twice weekly, filtered, and analyzed for elements of interest by ICP. The redox potentials of the samples were determined at sampling using a platinum (Pt) electrode and a Ag/AgCl reference electrode. The study was run in duplicate (subsamples A and B).

Table 1. Methods for determining soluble, acid-extractable, and total As.

Fraction	Extractant	Soil/Extractant Ratio	Extraction Time
H ₂ O-soluble	0.005M Ca(NO ₃) ₂	1:10	16 hr
Acid-extract.	0.1M HCl	1:10	1 hr
Total metal	Hot HNO ₃	1:20	6 hr

The samples chosen for this study contained high levels of total As. One sample was chosen from core A1: A1-1 (0.15 m depth); and two from core A2: A2-2 (0.45 m depth) and A2-5 (1.35 m depth).

RESULTS

Water Analysis

The results from the water analyses at the Kolin As dipping vat are presented in Table 2. The pH of the samples was near neutral. The soluble ($<0.45 \mu\text{m}$) As content of the water within the vat and of the groundwater at core A1 exceeded the EPA drinking water criteria for As of $0.050 \text{ mg}\cdot\text{L}^{-1}$ (USEPA, 1976). It appears that some of the As solution used in the vat still remains in the vat. The elevated concentration of As in the groundwater indicates that As has migrated into the subsoil either from a crack in the wall of the vat or from overflow, spillage, and drippings from livestock at the soil surface.

Soil Physical and Chemical Characteristics

The pH distribution with depth in the soil is shown in Figure 3. The pH ranged from pH 5 to near pH 8 at the soil surface. The high pH in the B cores was possibly due to something spilled or stored (eg, lime) on this site at some time in the past. The pH was lowest in all cores at the 1.5 m depth. The background samples from across the road showed lower pH values at each depth than the near-vat samples.

The CEC of the soil increased with depth (Figure 4). Very low ($<0.5 \text{ cmol}(+)\cdot\text{kg}^{-1}$) values were observed at the surface, but increased as much as 10-fold at 2.2 m.

Table 2. Water analysis for Kolin As dipping vat.

Sample	pH	As, mg•L ⁻¹
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Groundwater - core A1	7.15	0.3231
Dipping vat water	6.89	0.1403

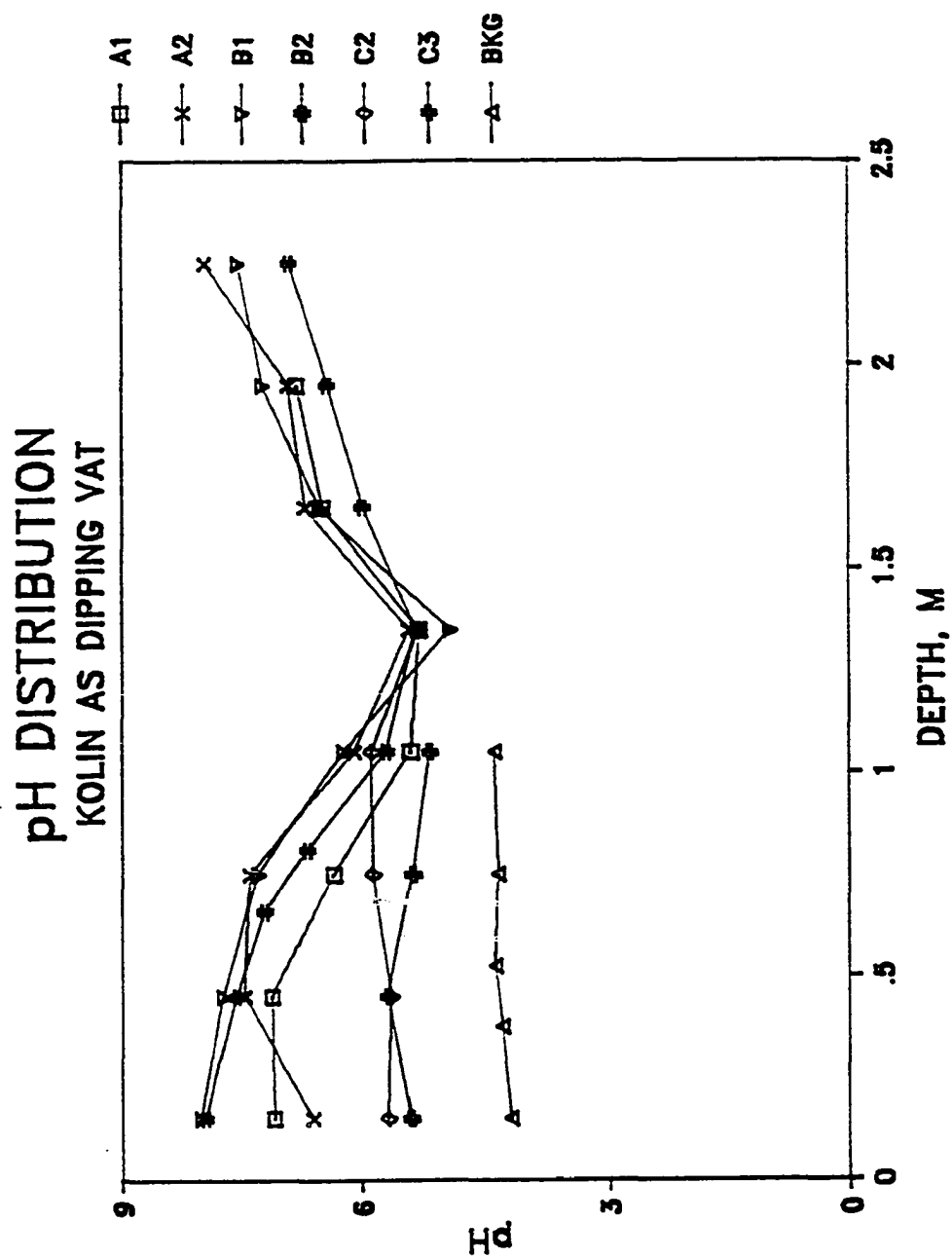


Figure 3. Soil pH with depth at Kolin As dipping vat.

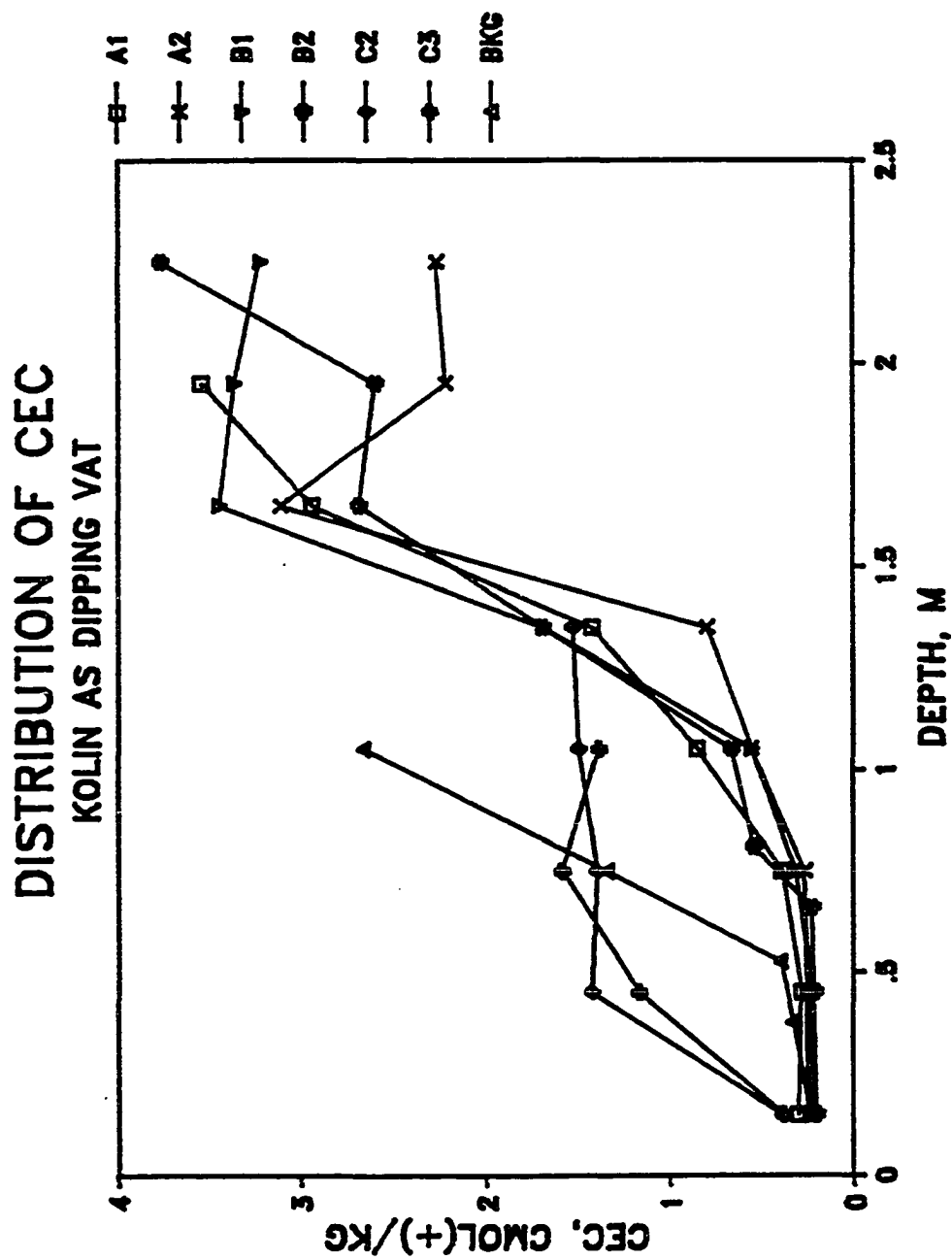


Figure 4. Cation exchange capacity (CEC) with depth at Kolin As dipping vat.

The particle-size distribution with depth was highly variable (Figures 5 and 6). The soil tended to have slightly more clay than sand.

The distribution of Mn oxides with depth, presented in Figure 7, shows higher levels in the upper 0.5 m and at 1.5-2.0 m. All levels of Mn oxides are fairly low, however, being $<0.05\%$ MnO_2 except in one sample.

The soil contained greater quantities of amorphous Fe oxides than Mn oxides (Figure 8). Again, greater quantities of the oxides were found in the upper 0.5 m. The A cores showed an increase in the oxide level at the 1.4 m depth.

The free Fe oxide content tended to peak at about the 1 m depth (Figure 9), although some cores had higher levels of these oxides at the surface. Near the 2 m depth of the A2 and B1 cores, there was an increase in the free Fe oxide levels.

The ranges of the soil characterization data from Cores A, B, and C in the contaminated areas are summarized in Table 3.

Chemical Forms

The distribution of water-soluble As with depth is given in Figure 10. Elevated levels of As were found in cores A1, A2, and B2 at or near the surface of the soil, compared to deeper samples and the background core. Core A2 showed elevated levels of As at depth, possibly as a result of leaching or due to a crack in the concrete liner as will be discussed below.

The As dipping vat contributed large amounts of HCl-extractable As to the soil, even at a depth of 1.5 m (Figure 11). The same As levels versus depth trends were seen for both H_2O -soluble and HCl-extractable As.

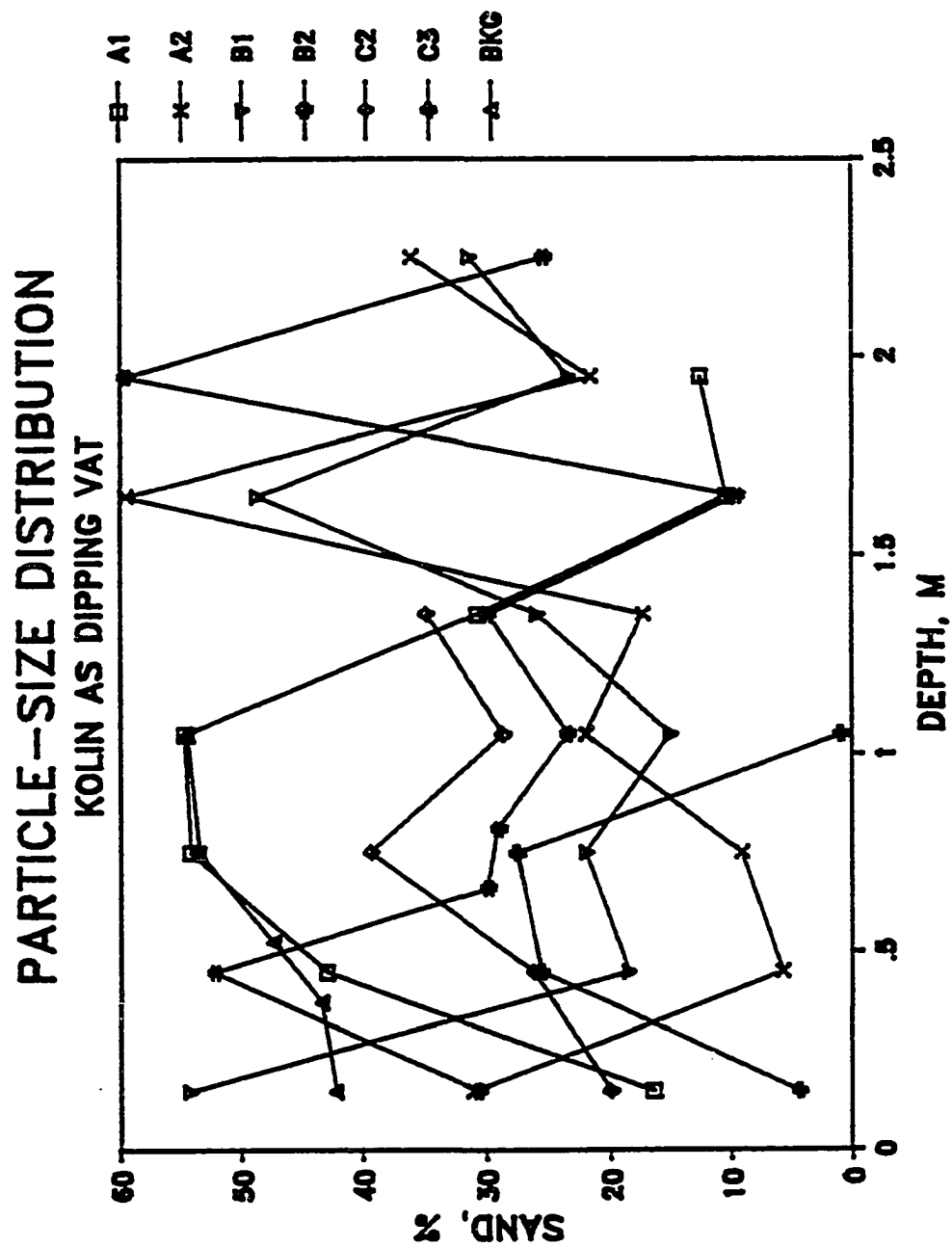


Figure 5. Sand content with depth at Kolin As dipping vat.

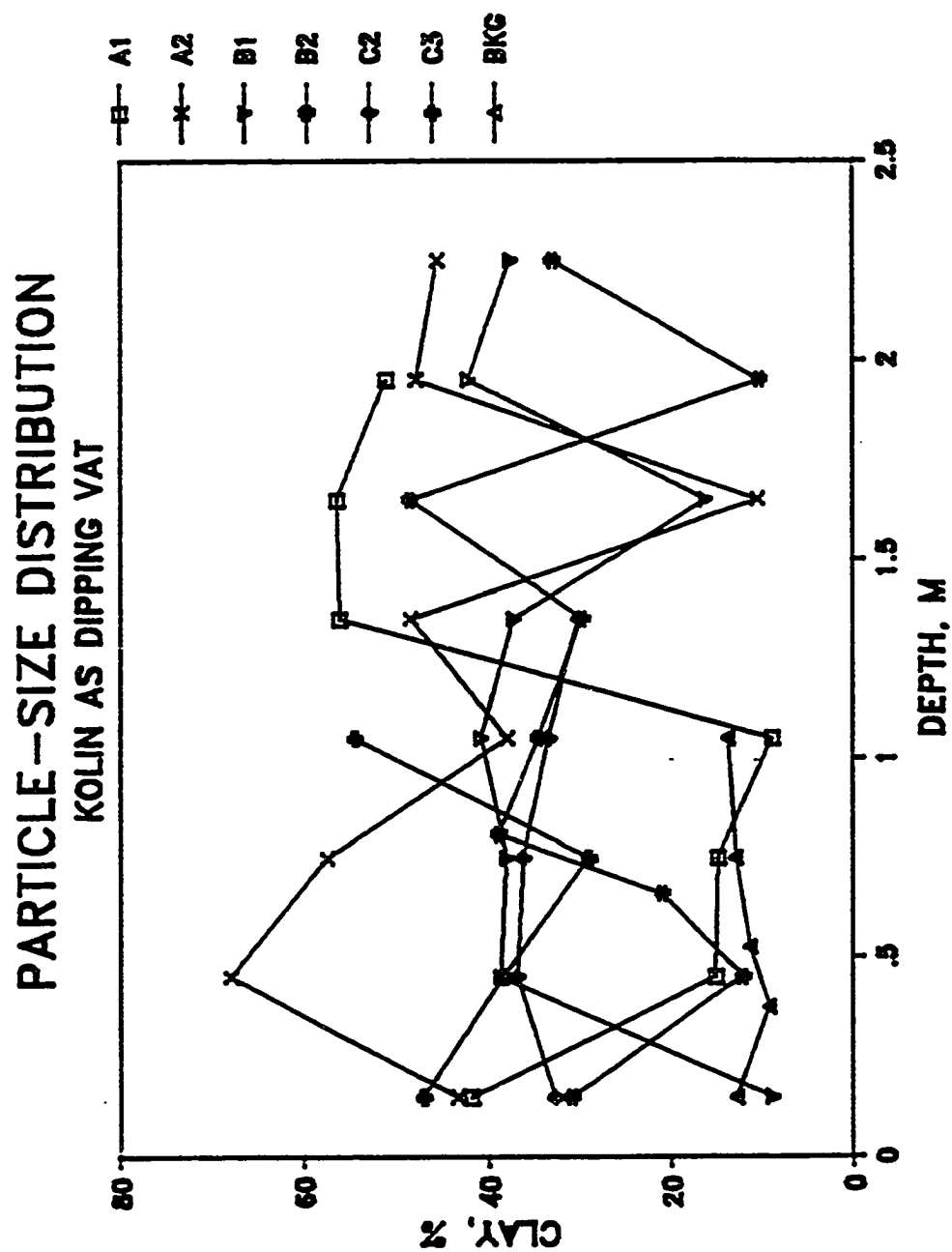


Figure 6. Clay content with depth at Kolin As dipping vat.

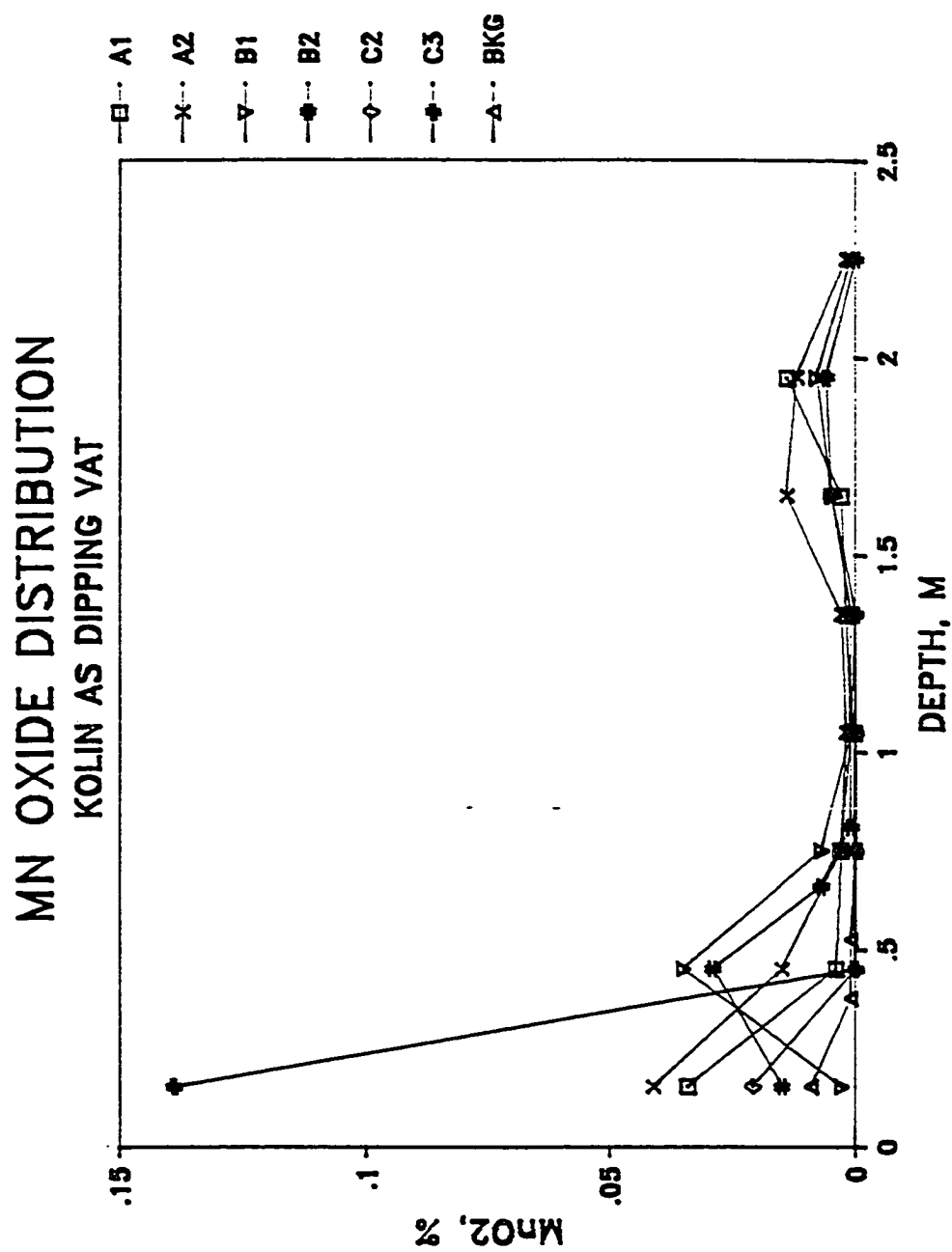


Figure 7. Manganese (Mn) oxide content with depth at Kolin As dipping vat.

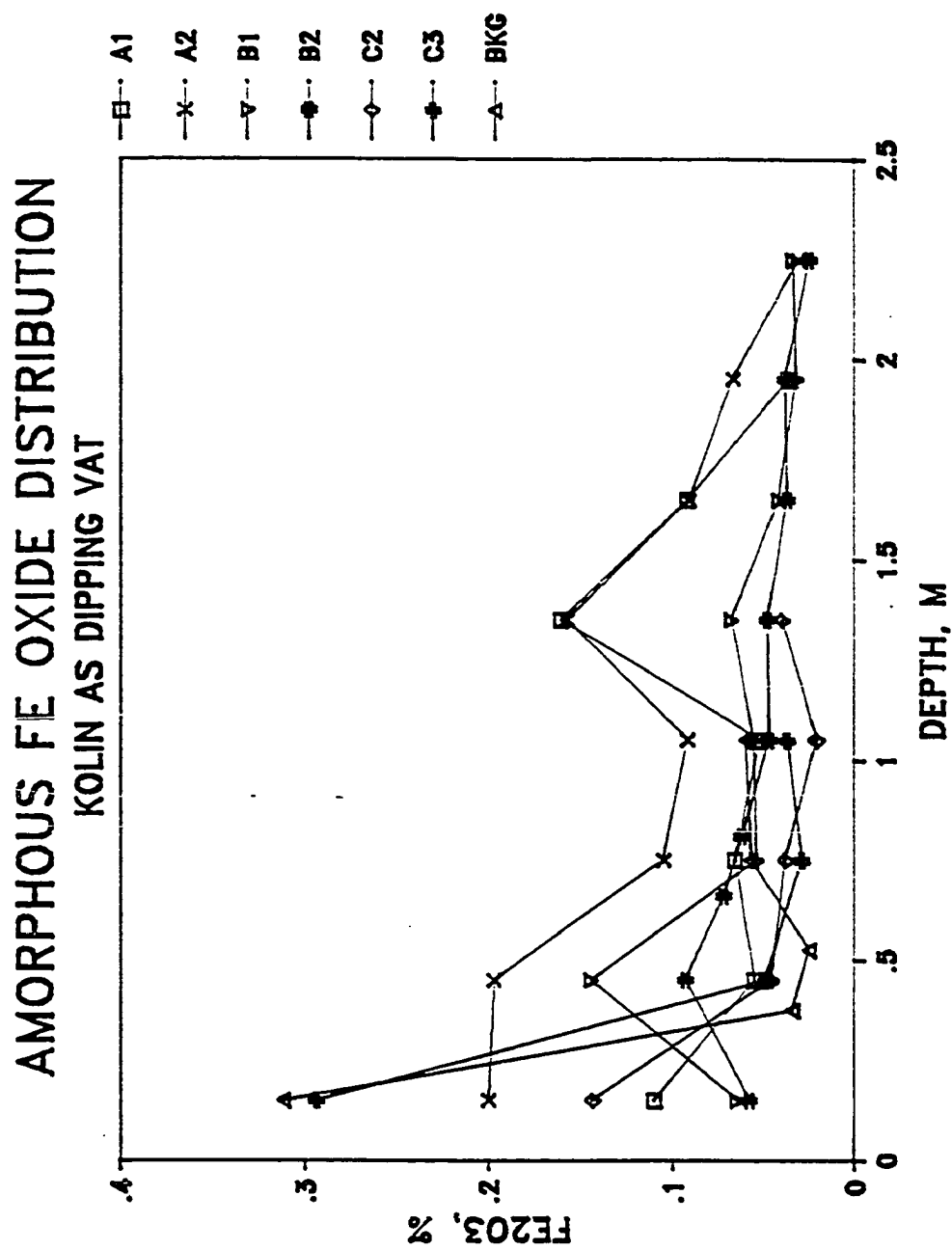


Figure 8. Amorphous iron (Fe) oxide content with depth at Kolin As dipping vat.

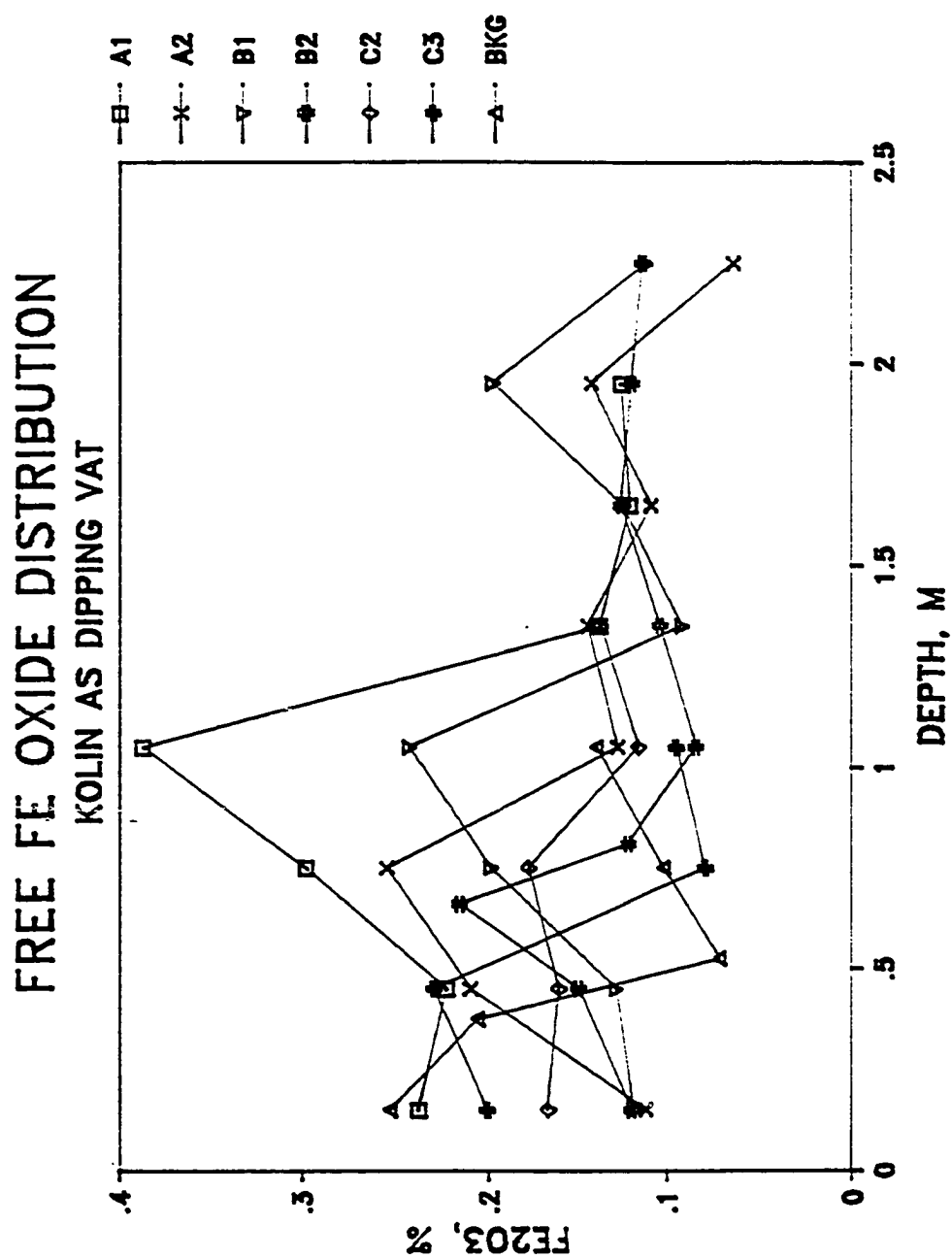


Figure 9. Free iron (Fe) oxide content with depth at Kolin As dipping vat.

Table 3. Soil characterization data from the Kolin As dipping vat.

Property	Range in Contaminated Areas
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Soil pH	4.5 - 8.2
CEC, $\text{cmol}(+)\cdot\text{kg}^{-1}$	0.2 - 3.8
Mn oxides, % MnO_2	0.000 - 0.14
Amorph. Fe oxides, % Fe_2O_3	0.025 - 3.1
Free Fe oxides, % Fe_2O_3	0.075 - 3.95
Soil texture	silty clay - sandy loam

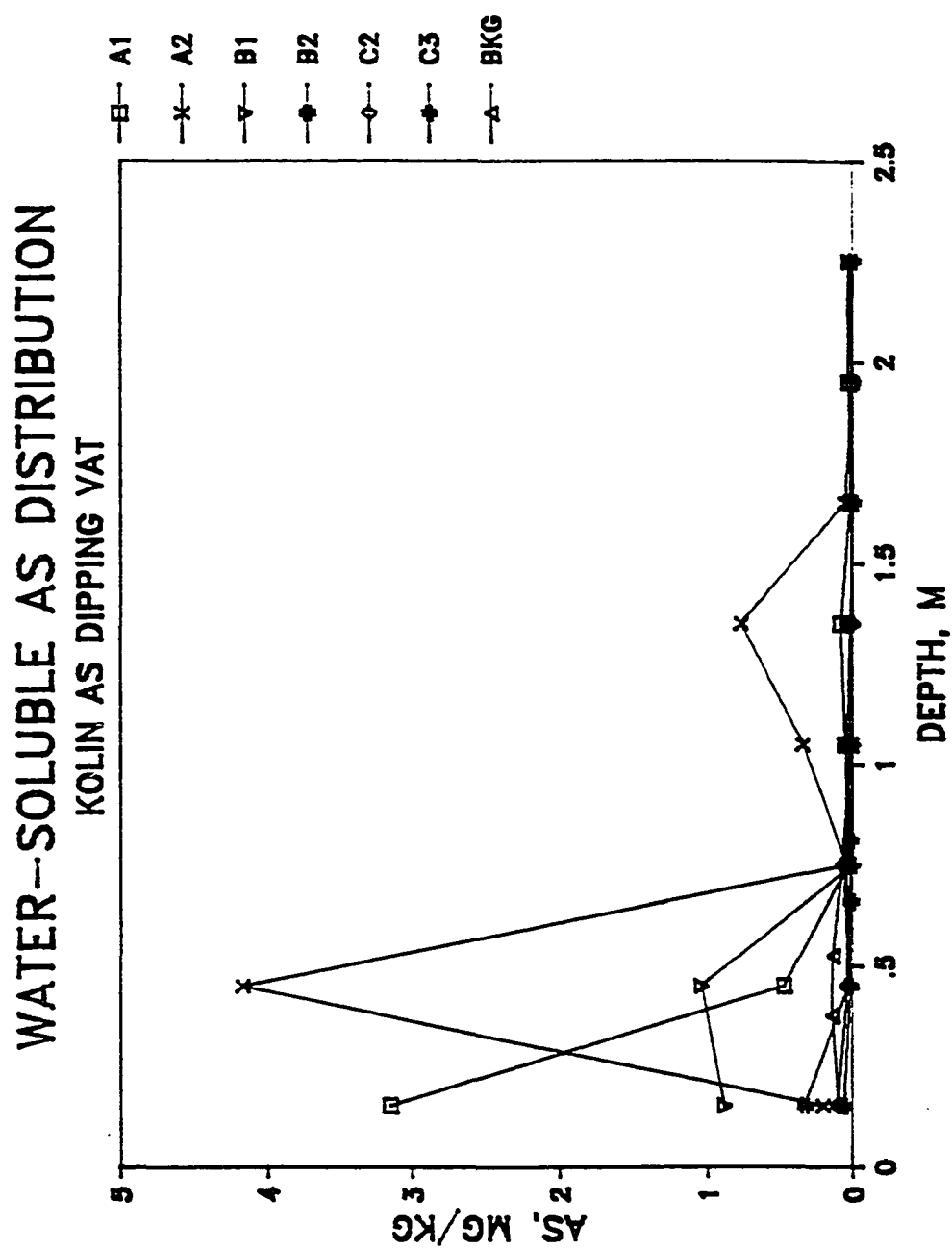


Figure 10. Water-soluble As with depth at Kolin As dipping vat.

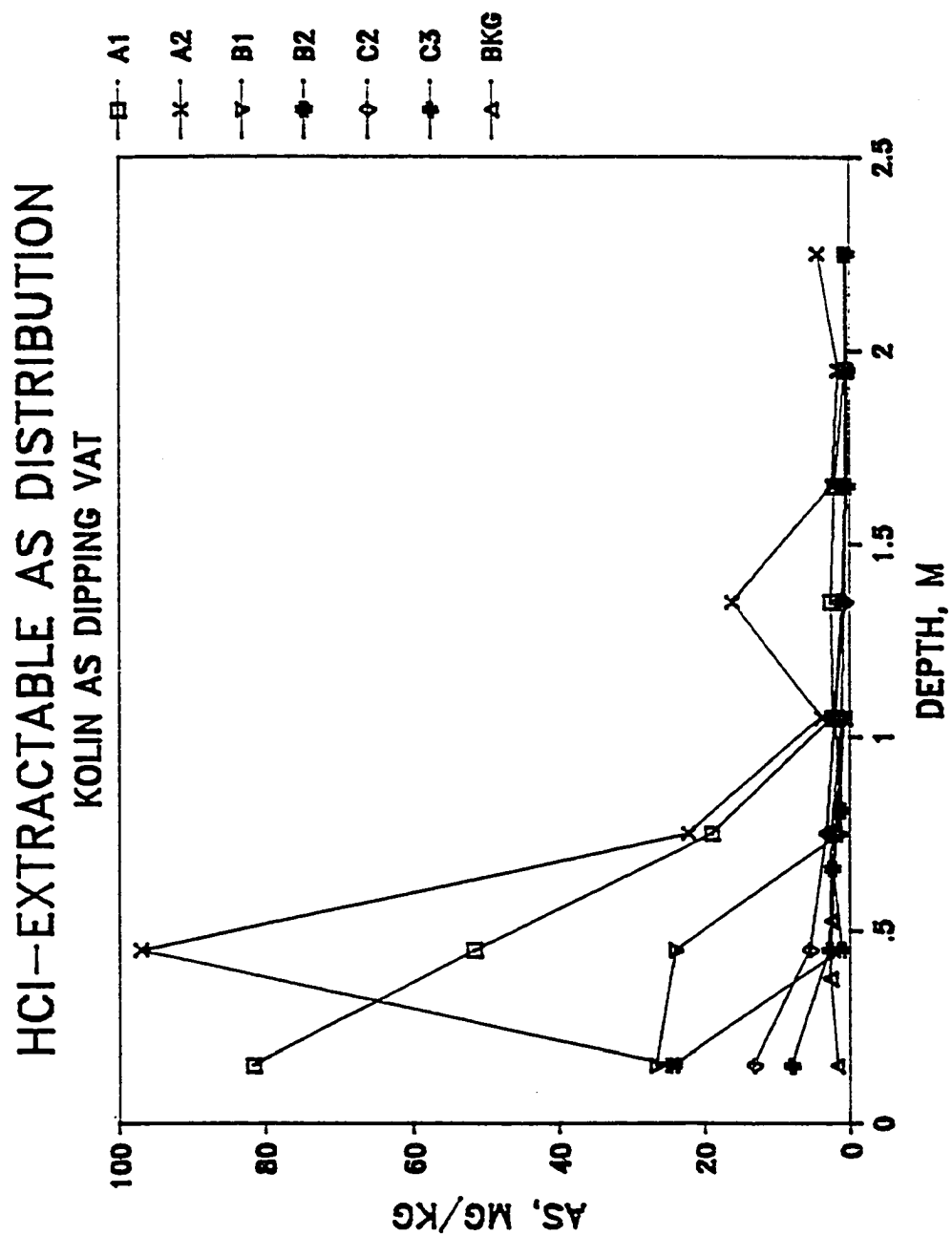


Figure 11. HCl-extractable As with depth at Kolin As dipping vat.

The distribution of total As with depth is given in Figure 12a-15a. Very high levels of As were observed at and near the soil surface. Most of the As is within the upper 1 m of the soil. It appears that some As is being transported through the soil by leaching. Although there was a large drop in As levels below 0.75 m, As values at depths up to 2 m exceeded background levels.

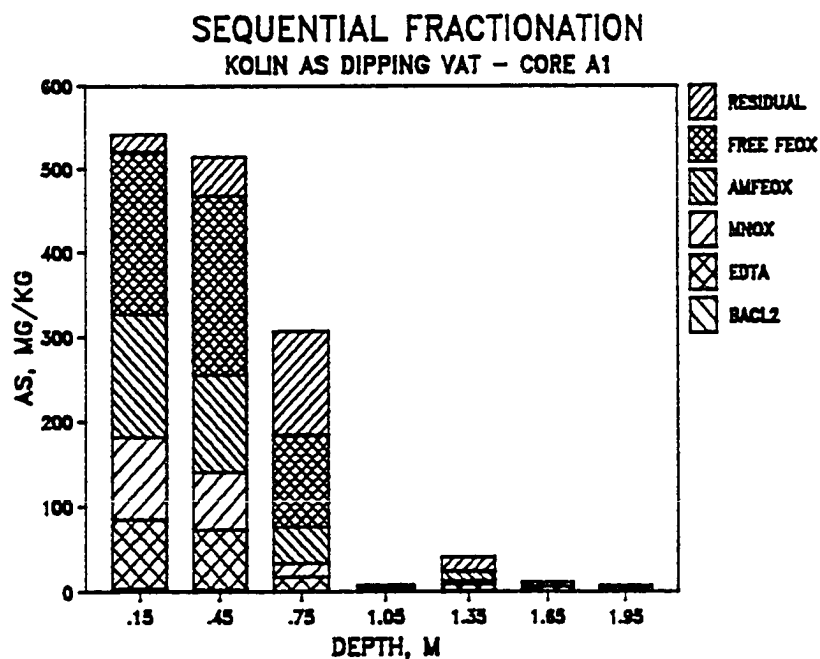
The results from the sequential fractionation scheme for one core of each pair of cores will be presented for illustration. Examining the results from core A1 (Figure 12b), the "available" As (BaCl_2 + EDTA fractions) was least at the surface where no exchangeable As was found. The oxide fractions were very important in As retention. The available As tended to follow the trend in amorphous Fe oxides. Arsenic associated with free Fe oxides was only found in the upper 0.75 m of the soil. Where there was little As associated with free Fe oxides (below 1 m), the As was more available.

Very similar results were found for core B1 (Figure 13b). The available As was low at the surface, with only a minor fraction of exchangeable As. The oxides, particularly free Fe oxides, were important at the shallow depths. Below 1 m, at least 60% of the As was available, with the remaining As mostly retained by amorphous Fe oxides.

Core C2 (Figure 14b) again showed the same associations with depth-increased availability of As where oxide contents were lowest.

For the background core, where As levels were low, approximately 60% of the As was available. The other 40% was mostly in the amorphous Fe oxide phase with a small amount associated with Mn oxides.

(A)



(B)

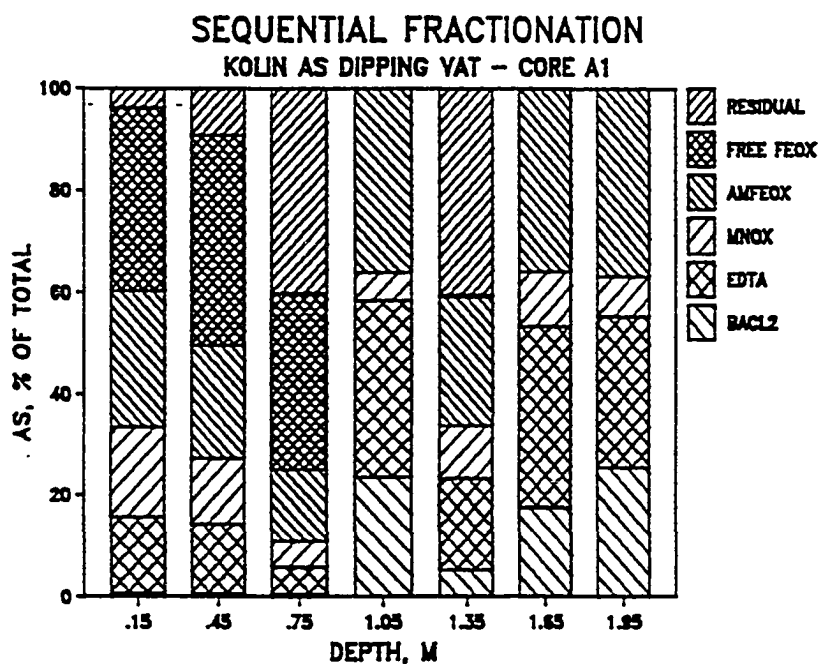
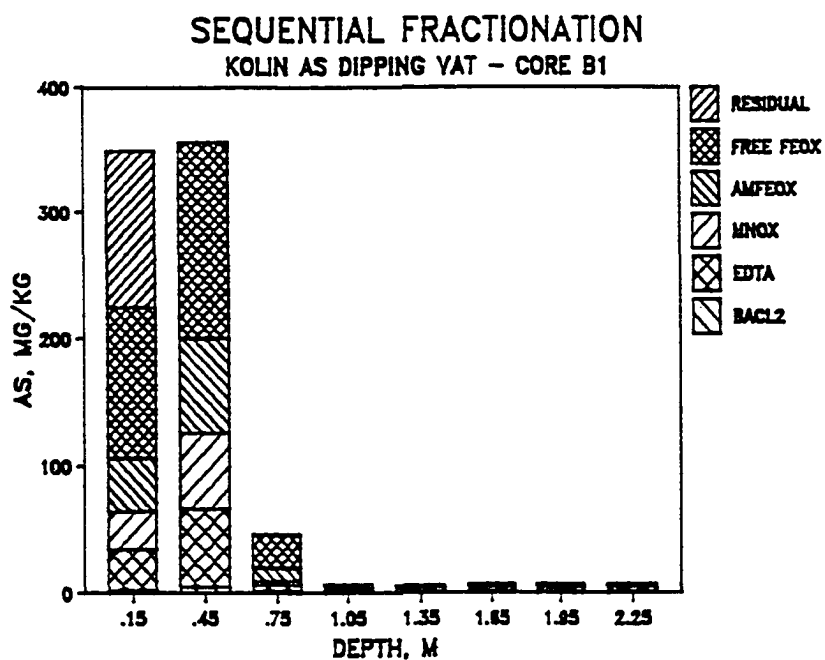


Figure 12. Distribution of As with depth between chemical forms in Core A1 at Kolin As dipping vat.

(A) Concentration

(B) Percent of total

(A)



(B)

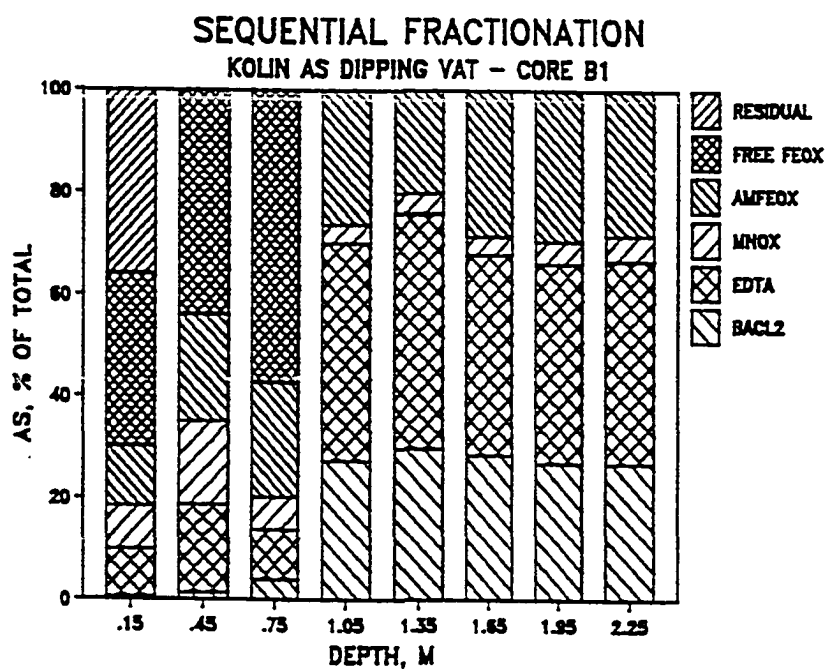
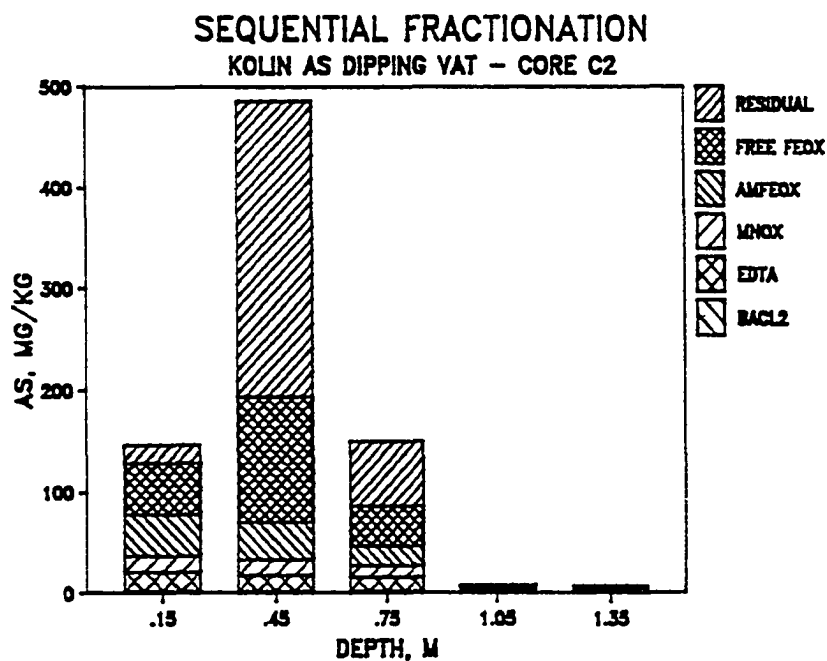


Figure 13. Distribution of As with depth between chemical forms in Core B1 at Kolin As dipping vat.

(A) Concentration

(B) Percent of total

(A)



(B)

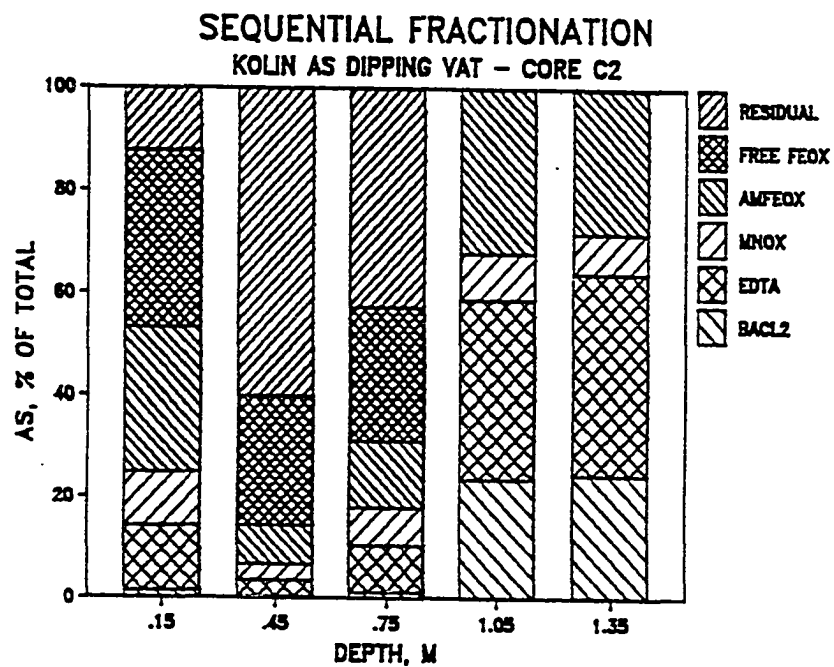


Figure 14. Distribution of As with depth between chemical forms in Core C2 at Kolin As dipping vat.

(A) Concentration

(B) Percent of total

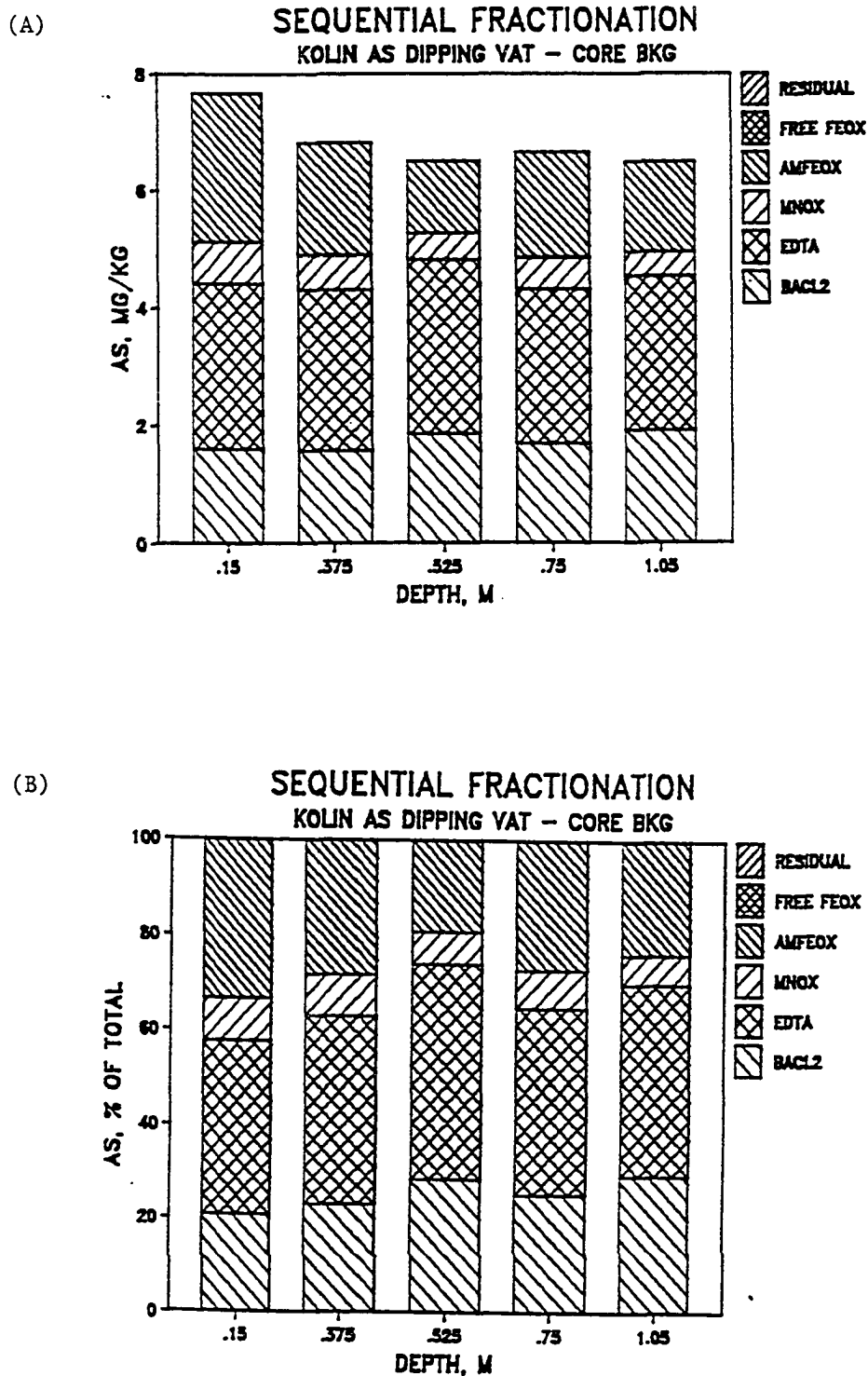


Figure 15. Distribution of As with depth between chemical forms in the background core at Kolin As dipping vat.

(A) Concentration

(B) Percent of total

Long-Term Release of As

For the surface soil sample (KA1-1), the As that was initially released from the soil was slowly readsorbed during the two-month study (Figure 16). Arsenic was released over time from the subsurface samples (KA2-2 and KA2-5). The sample from the deepest depth (KA2-5) released very little As (it contained very little As), although this release was continuous over the two months.

Iron (Figure 17) and Mn (Figure 18) were released during the two months from the KA2-5 samples. The other samples released very little Fe and Mn during the study.

The redox potential generally decreased during the Ar purging and increased during the second air purging (Figure 19), indicating that the purging gas influenced the redox potential to some degree in the soil samples.

DISCUSSION

Chemical Forms

Elevated levels of As at the shallow depths and at 1.35 m for cores A1 and A2 corresponded to higher Mn oxide and amorphous Fe oxide levels. These oxides may be responsible for retaining the As at these depths and preventing it from leaching out of the soil sampling area. The importance of the oxides can also be observed in the sequential fractionation results. Where there were elevated levels of As, the As retained by the oxide phases is greater than where the levels of As were low.

These results are supported by other research findings. Page and Pratt (1975) proposed that in acid soils, as at Kolin, dissolved As

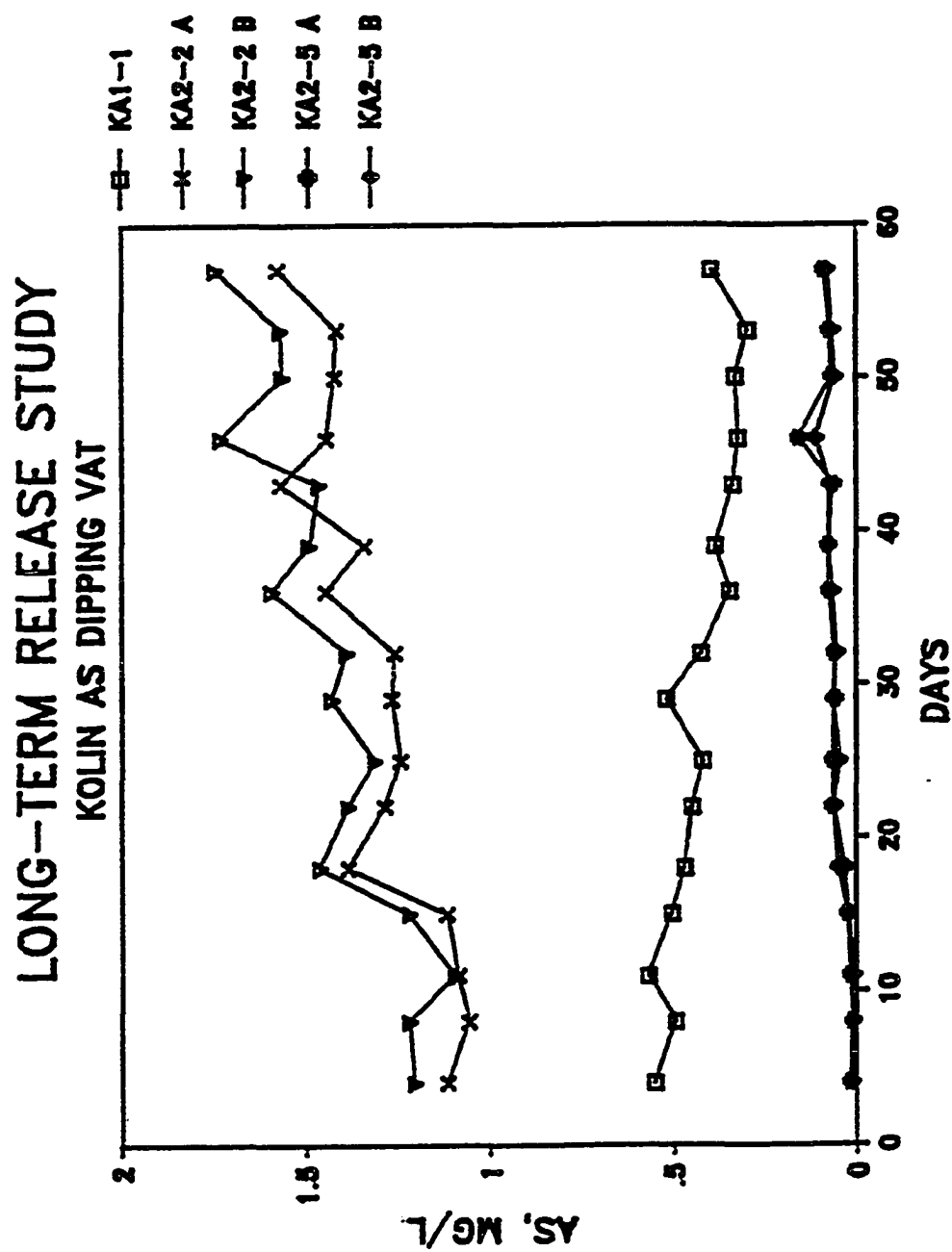


Figure 16. Release of As over time from selected contaminated soil samples from Kolin As dipping vat.

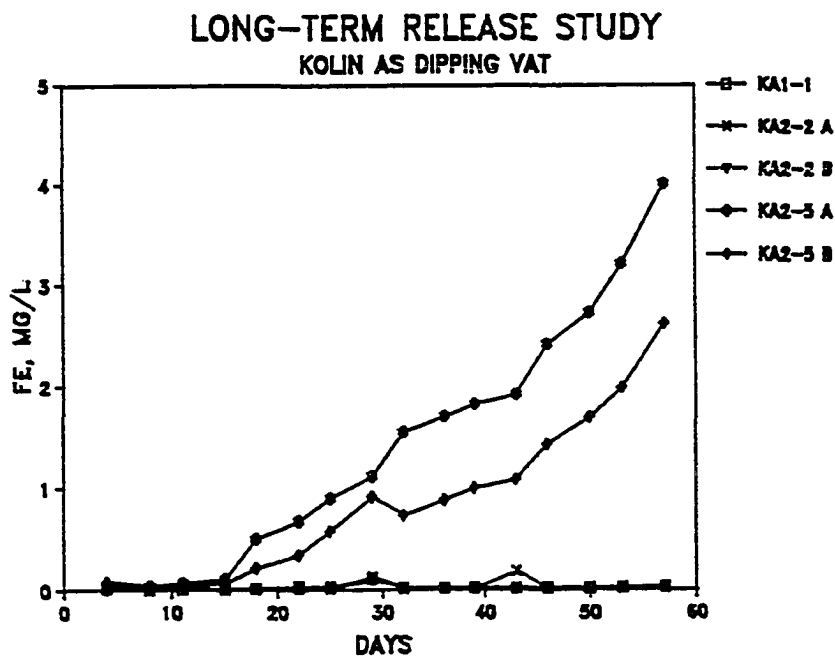


Figure 17. Release of Fe over time from selected contaminated soil samples from Kolin As dipping vat.

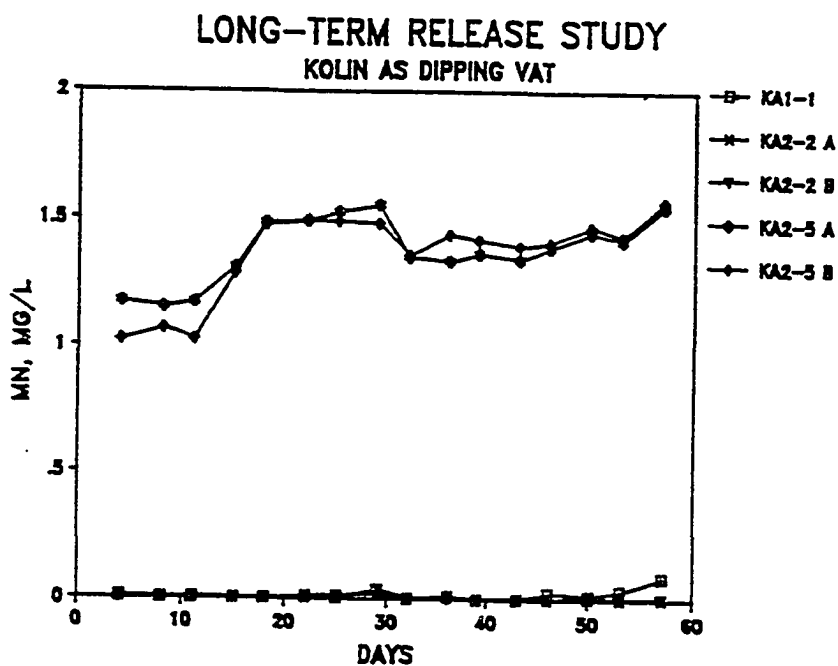


Figure 18. Release of Mn over time from selected contaminated soil samples from Kolin As dipping vat.

LONG-TERM RELEASE STUDY KOLIN AS DIPPING VAT

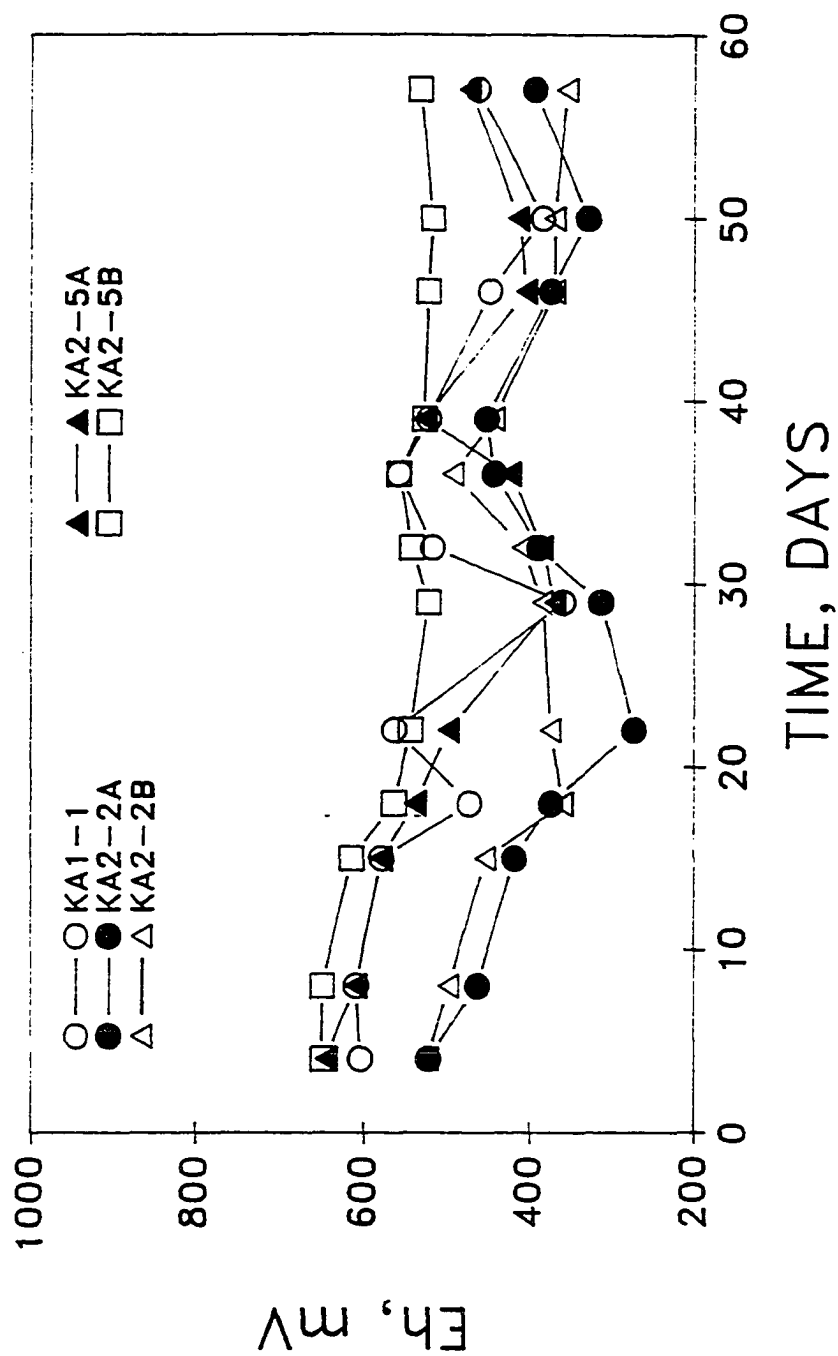


Figure 19. Redox potential versus time during long-term release study.

probably reacted to form insoluble Fe and Al arsenates. Livesey and Huang (1981) reported that arsenate retention was predominately by the poorly crystalline hydroxy-Fe and hydroxy-Al compounds of recent weathering. Fuller (1978) found a correlation between anion metal retention and free Fe oxides.

Gruebel et al. (1988), working with minerals, reported that little As was found in solution after extraction of the amorphous Fe oxide phase. They concluded that there was readsorption of As by phases unaffected by the extractant. Thus, the As in the amorphous Fe oxide phase would be underestimated. This did not seem to occur in the Kolin soil samples since most of the As was accounted for, especially at the deeper depths. The amorphous Fe oxide phase was often quite large compared to other phases.

At deeper depths, the As was present at lower concentrations but in more available forms. It is possible that the As was leached from these lower depths due to lack of oxides for retention, or the lower As concentration may be due to lack of leaching from higher in the profile where oxides bound the As effectively. The possibility of leaching from the lower depths is supported by the long-term release study. Proportionally less As was released from the samples taken at shallow depth, where the oxide content was greater, than from the deeper samples.

Holm et al. (1979) fractionated As in reducing sediments and reported that the As occluded in amorphous weathering products was much greater than exchangeable As. Similar results were found in the surface samples at Kolin. At deeper depths, however, the exchangeable phase was as large as the amorphous oxide phases.

Correlation Between Extractable As and Soil Properties

Simple correlation coefficients between various forms of extractable As and selected soil properties were determined (Table 4). Extractable As was correlated with pH, Mn oxide content, amorphous Fe oxide content, free Fe oxide content, and CEC. These correlations agree with the results of the extraction work. Also, Fuller (1978) found a slight pH effect on As retention. The extractable As was correlated best with the amorphous Fe oxides and CEC. One of the best correlations was between As associated with the amorphous Fe oxides and the amorphous Fe oxides content of the soil. This indicates that the As extracted was for the most part actually associated with the amorphous Fe oxides. This is counter to the results of Gruebel et al. (1988) who concluded that the amorphous Fe oxide-extractable As was underestimated due to readsorption by other minerals unaffected by the extractant. The As extracted with the Mn oxides was weakly but significantly correlated with the percent Mn oxides but was more highly correlated with the percent amorphous Fe oxides. Because the two extractants for the oxides are very similar, it is likely that the Mn oxide extractant was extracting some of the As associated with the amorphous Fe oxides. As stated previously, the As extracted with the amorphous Fe oxides was a very important fraction of the As in the soil.

For the surface horizons, HCl-extractable As was correlated with Mn oxide and amorphous Fe oxide (Table 5), again indicating the importance of the oxide phases in As retention.

Table 4. Simple correlation coefficients relating extractable As to soil properties - Whole soil.

Fraction	pH	MnOx	AmFeOx	FreeFeOx	CEC
H ₂ O-soluble	0.319*	ns	0.396*	ns	-0.322*
HCl-extract.	-0.348*	ns	ns	ns	-0.349*
BaCl ₂ -extract.	0.433**	ns	0.425**	ns	ns
EDTA-extract.	0.413**	ns	0.446**	ns	-0.469**
Mn oxide-assoc.	0.399**	0.313*	0.443**	ns	-0.480**
Amorph. Fe oxide-assoc.	0.336*	0.432*	0.545**	0.341*	-0.531**
Free Fe oxide-assoc.	0.385*	ns	ns	0.310*	-0.524**
Residual	ns	ns	ns	0.334*	ns
Total	0.390*	ns	0.418**	0.315*	-0.523**

*, ** significant at 0.05 and 0.01 levels, respectively.

ns = not significant.

Table 5. Simple correlation coefficients relating extractable As to soil properties - Surface only.

Fraction	Mn oxide	Amorph. Fe oxide
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HCl-extract. As	0.954**	0.918**

All other fractions were not significantly related to Mn oxides or amorphous Fe oxides.

not significant: extractable As with pH, free Fe oxides, CEC, or particle size.

** significant at 0.01 level.

CONCLUSIONS

Higher concentrations of As were found at the soil surface and at shallow depths. Fractionation of As varied with depth suggesting possible changes in the form of As. Arsenic was more available below 0.75 m. The oxide fractions, particularly amorphous Fe oxide, were important in As retention. Significant correlations between extractable As and pH, CEC, and metal oxides were observed. Long-term release studies showed only a slight increase in As solubility over time, indicating low mobility of As.

During the many years of use, it is likely considerable amounts of As spilled or splashed out of the vat onto the surface of the ground near the vat. Thus the elevated As levels found at the 1.5-m depth in one core may have leached from the surface. However, a crack in the concrete wall (possibly extending to the bottom) may have allowed relatively concentrated As solution to enter the soil a meter or more beneath the surface. At the time of sampling, the vat was holding water at an elevation considerably above groundwater levels. It is not possible now to obtain any kind of estimate on when the crack occurred, the amount of As that may have moved through the crack over the years, or even whether the leak rate (if ever it did leak) is greater or less than it was in previous years.

It should be noted that the history of use of this vat is not known and the first sampling occurred about three decades after use was discontinued. Therefore, it is possible that considerable As has been transported from the site during the intervening years for which there is no current evidence. Since maximum As levels were in the shallow subsoil versus deeper subsoil, the data suggest that most of the As associated

with the pit may be retained strongly by the soil such that leaching beneath at least a couple of meters may have been negligible. With As in particular, however, speciation from various possible redox transformations may have allowed substantial As to leach through the profile while present concentration peaks, possibly as different species, remain near the surface. Thus, it is not possible to know what occurred at this point in time. Speciation of As at this site is warranted to further elucidate possible mechanisms of As transport.

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CHAPTER 4

THE DISTRIBUTION AND ENVIRONMENTAL CHEMISTRY OF METALS
IN SOIL AT AN INDUSTRIAL WASTE SLUDGE LAGOON

ABSTRACT

The distribution and environmental chemistry of metals in soil at a former industrial waste disposal site was examined to determine the factors affecting metal mobility in subsoils. Levels of Cd, Cu, Pb, and Zn in soil samples from the Robins AFB site indicate very high levels of contamination. Of the more than 25 samples obtained from the disposal site cores and just outside the disposal zone, eight contained about 100 $\text{mg}\cdot\text{kg}^{-1}$ or higher levels of Cd (Cd ranged to more than 900 $\text{mg}\cdot\text{kg}^{-1}$), six contained about 100 $\text{mg}\cdot\text{kg}^{-1}$ or higher levels of Cu (Cu ranged to 550 $\text{mg}\cdot\text{kg}^{-1}$), four contained more than 100 $\text{mg}\cdot\text{kg}^{-1}$ Ni (Ni ranged to near 250 $\text{mg}\cdot\text{kg}^{-1}$), 14 contained about 200 $\text{mg}\cdot\text{kg}^{-1}$ or higher levels of Pb (Pb ranged to more than 2700 $\text{mg}\cdot\text{kg}^{-1}$), and 13 contained about 200 $\text{mg}\cdot\text{kg}^{-1}$ or higher levels of Zn (Zn ranged to more than 1400 $\text{mg}\cdot\text{kg}^{-1}$). The spatial distribution of metals indicated pockets of contamination, due either to deposition or vertical migration.

Cadmium retention was predominately by the amorphous Fe oxide fraction. The three oxide fractions, Mn oxides and amorphous and free Fe oxides, were important in Cu and Pb retention. Much of the retained Pb

and Ni was not recovered in the selective extraction procedure. Of the extractable Ni, the free Fe oxide fraction and the amorphous Fe oxide fraction were the dominant forms. The amorphous Fe oxide fraction was most important in Zn retention, followed by the free Fe oxide fraction.

The samples obtained from Robins AFB were highly contaminated with what we were told was a mixture of hazardous organics. This organic waste mixture has the potential for affecting metal chemistry and transport, creating a very complicated system. The core from an adjacent area between the sludge disposal pit and the surrounding swamp (E core) was also saturated with the same oily liquid as the pit samples, and also contained some of the highest metal levels. If information provided us that our Core E samples were taken out of the sludge disposal area is correct, then the data indicate movement of high concentrations of several metals has occurred in the shallow groundwater at this location. This movement was likely facilitated by sandy soils and/or high levels of organic and other wastes present. Long-term laboratory release studies indicated that Cd, Pb, and Zn could be mobilized over time.

INTRODUCTION

The transport of metals to groundwater below hazardous waste sites is of great environmental concern. The migration of trace elements through soils depends upon the properties of the leaching solution, the soil, and the trace element. The physical properties of the leaching solution (i.e., specific weight, viscosity, surface tension) determine the mobility of the individual components and their miscibility (Jackson, 1980). The chemical properties of the leaching solution (i.e., pH, total

organic carbon, chemical oxygen demand, carbon dioxide tension, soluble inorganic salts, total soluble Fe content, specific polluting element concentration, age of leachate, and amount and strength of organic chelates and inorganic complex ion formers present) also affect the mobility of trace elements.

The trace metals must be in the soluble phase or associated with mobile particulates to be transported through soil. Therefore, various soil factors, such as bulk density, surface area, particle-size distribution, pH, redox status, ion exchange capacity, amount of organic matter, and type and amount of clay minerals, affect metal migration through soil (Amacher et al., 1986).

An unlined industrial waste lagoon with the bottom excavated below the water table level, such as at Robins AFB, Warner Robins, Ga., has the potential for metal contamination of surrounding soil and groundwater. The mixture of industrial wastes could accelerate metal movement by complexing the metals, preventing retention by soil constituents. Because the lagoon bottom is below the water table level, lateral movement through the groundwater to surrounding areas is also possible.

The objectives of this study were: (1) to determine the distribution of metals in soil cores at an industrial waste sludge lagoon; (2) to determine the quantities of metals associated with specific mineral phases using a sequential extraction scheme; and (3) to determine long-term metals release from metals-contaminated soil under alternating oxidizing/reducing conditions.

MATERIALS AND METHODS

Site Descriptions

Robins AFB, located in Warner Robins, Ga., is an Air Force logistics base. Between 1965 and 1978, general refuse and occasionally industrial wastes were disposed of in Landfill No. 4. A sludge lagoon, encompassing 0.6 ha and located on the north end of Landfill No. 4, was used for disposal of industrial wastewater treatment plant sludges (2%-5% solids) from approximately 1962 until its closure in 1978. The lagoon was an unlined, diked pit with the bottom excavated below the water table level (Radian Corp., 1985). The industrial wastes were believed to contain phenols, oils, cyanide, chromium and other heavy metals, solvents, hydraulic fluids, and paint removers (Radian Corp., 1985). The landfill was covered daily with a sandy soil and the entire area capped with sandy loam soil after closure.

The soil at the landfill is described as a swamp soil, a perennial wetland soil. The background sample obtained from the area as a control location was a Norfolk loamy fine sand (fine-loamy, siliceous, thermic, Typic Paleudult) with a typical permeability of 1.6 to $>16 \text{ cm} \cdot \text{hr}^{-1}$. It should be noted that for this site's control soil, the soil material was likely not the same as the waste-site soil due to our inability to collect cores within the surrounding swamp.

A preliminary study of the disposal site was performed by Radian Corp. (1985). Results of analyses of samples collected in the vicinity of the lagoon indicate that most of the metal concentrations were within the range typically found in soils (Baker and Chesnin, 1975). Soluble Ni in an upgradient well and in one well in the pit exceeded the EPA drinking

water criterion ($13.4 \mu\text{g}\cdot\text{L}^{-1}$) (Radian Corp., 1985). Because there were no long-term, background data for the study area, Radian Corp. (1985) could not determine whether these concentrations of metals in the soil were indicative of natural conditions. Vertical hydraulic gradients in the area favored discharge of groundwater from the disposal area into surface water of the swamp (Radian Corp., 1985).

Sampling Procedures

Soil cores were obtained using commercial equipment that hydraulically presses a stainless steel core extractor tube (4.75 cm diameter) into the ground. Single cores were obtained from the area receiving waste and adjacent to the swamp (Figure 1). Core A was obtained approximately 15 m southeast of the hauling road. Core B was taken approximately 15 m south of the hauling road. Core C was taken approximately 8 m southeast of the hauling road. Core D was obtained approximately 9 m south of the hauling road. Core E was obtained approximately 60 m southwest of the hauling road and was outside the sludge lagoon zone. According to information provided by Air Force personnel, Cores A through D were within the sludge disposal zone, and the E core was out of the sludge disposal zone. However, a black oily liquid was also found at a shallow depth associated with the latter core, possibly as a result of lateral subsurface flow.

It was impossible to obtain a clean, undisturbed background sample from near the swamp. Therefore, a separate site was chosen on the base within the Norfolk soil series.

After the cores were pulled to the surface, they were sectioned by depth and/or horizon and placed in 1-L plastic storage bottles. The

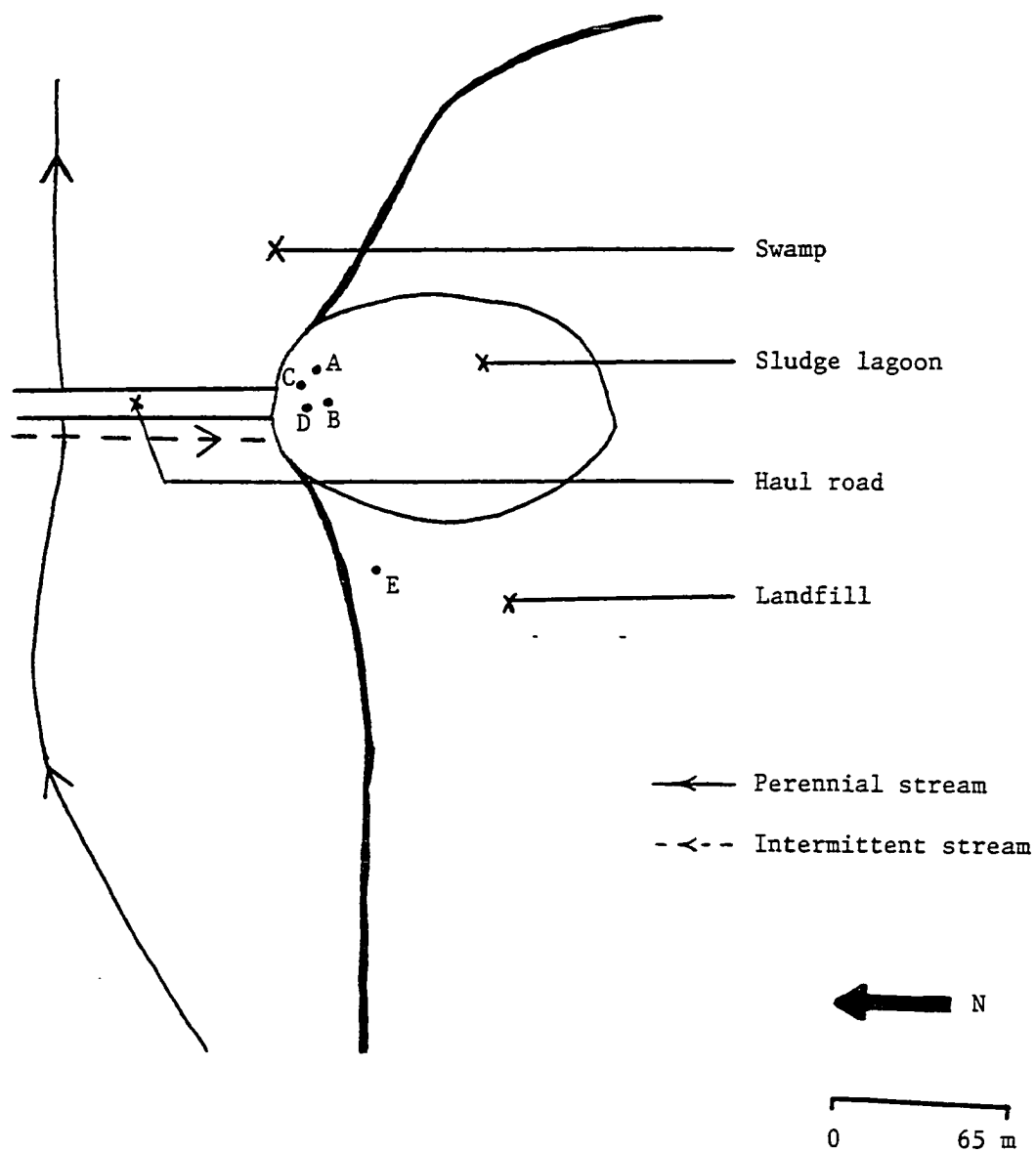


Figure 1. Location of cores samples at Robins AFB, Warner Robins, Georgia.

samples were refrigerated upon return to the laboratory to preserve conditions found in the field.

Chemical Forms

The soil samples were extracted to determine selected chemical forms of metals in the soil using the sequential fractionation scheme outlined in Figure 2. This design is not based on any particular scheme in the literature, but is similar to several used by other investigators (Pickering, 1981; Salomons and Forstner, 1984). The scheme consists of running the procedures for extracting Mn oxides, amorphous Fe oxides, and free Fe oxides in sequence preceded by extractions with a neutral salt (BaCl_2) and a chelating agent (EDTA) to determine weakly and strongly sorbed metal. The extractants in the sequential fractionation scheme were intended to extract metals associated with the following chemical phases in soils: (1) 0.1M BaCl_2 - weakly sorbed and exchangeable metals; (2) 0.05M EDTA - strongly sorbed metals; (3) pH 2, 0.1M $\text{NH}_2\text{OH}\cdot\text{HCl}$ - metals associated with Mn oxides; (4) 0.25M $\text{NH}_2\text{OH}\cdot\text{HCl}$ -0.25M HCl - metals associated with amorphous Fe oxides; and (5) DCB - metals associated with free Fe oxides (crystalline Fe oxides + amorphous Fe oxides not extracted by extractant (4)). The BaCl_2 and EDTA extractants do not dissolve a particular mineral phase, thus metals sorbed to a variety of mineral phases including metal oxides can be extracted with these extractants. The metal oxide extractants extract strongly sorbed metals not extracted by the BaCl_2 and EDTA as well as metals coprecipitated with the metal oxides.

The total metals in the soil samples were determined on separate soil aliquots using a hot HNO_3 digestion (1:20 soil/extractant ratio; 16

SEQUENTIAL FRACTIONATION SCHEME

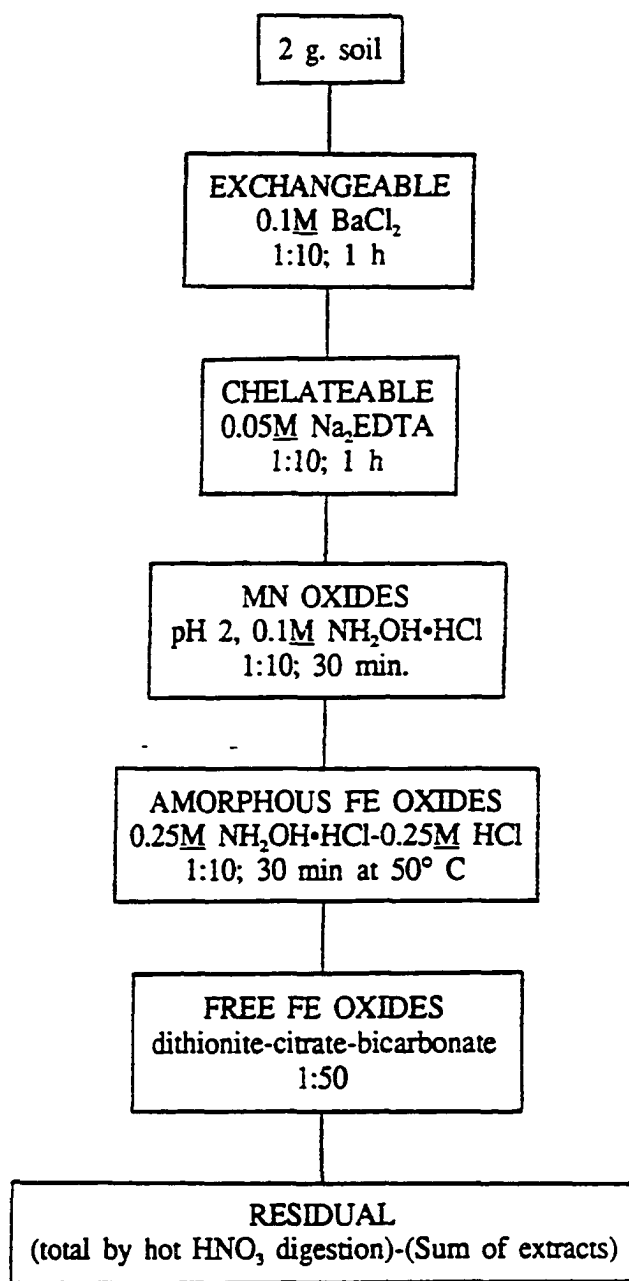


Figure 2. Sequential fractionation scheme used to determine the distribution of metals in the soil at Robins AFB.

h digestion). The residual fraction was determined by subtracting the sum of metal extracted by the sequential fractionation scheme from the total metal levels determined.

Long-Term Release of Metals

To determine if metals are being released over time and if this release is affected by changing redox conditions, 0.005M $\text{Ca}(\text{NO}_2)_3$ was added to selected contaminated soil samples from the site at a soil/solution ratio of 1:10 and continuously shaken on a reciprocating shaker at 140 $\text{osc}\cdot\text{min}^{-1}$. The soil/solution mixtures were purged daily with air (designated O_2 in text and figures) for two weeks, then with Ar for two weeks, then again with air for two weeks, then with Ar for two weeks using the experimental setup described in Chapter 6. The suspensions were sampled twice weekly, filtered, and analyzed for elements of interest by ICP. The redox potentials of the samples were determined at sampling using a platinum (Pt) electrode and an Ag/AgCl reference electrode. The study was run in duplicate (subsamples A and B).

The samples chosen for this study contained high levels of total metals. One sample was chosen from core A - A-6 (1.5 m depth); one from core C - C4 (1.05 m depth); and one from core E1 - E1-4 (1.3 m depth).

RESULTS

Chemical forms

To illustrate the levels of metals at this site, Table 1 lists the highest levels of each metal in each core and at what depth these high levels were found. These levels indicate significant metal contamination

Table 1. Highest levels of metals in cores at Robins AFB and depths at which they occur.

Core	Cd	Cu	Ni	Pb	Zn
	----- mg•kg ⁻¹ -----				
A	200(1.8m)	80(1.8m)	120(1.5m)	225(1.5m)	270(1.8m)
B	430(1.5m)	70(1.5m)	60(1.5m)	200(1.5m)	340(1.5m)
C	330(0.7m)	150(0.4m)	120(0.7m)	760(0.7m)	490(0.7m)
D	930(0.8m)	285(0.8m)	200(0.8m)	3700(0.8m)	1450(0.8m)
E	725(1.3m)	555(1.3m)	240(1.3m)	510(1.3m)	515(1.3m)

of soil. The total metal contents of Core A samples are shown in Figures 3-7 to illustrate the distribution of metals with depth in the soil at Robins AFB. The samples were contaminated with those metals typically found in metal-plating wastes (Cd, Cu, Ni, Pb, and Zn). The same trends are seen for each of the metals, showing the depths where there are pockets of contamination. Our samples indicate higher levels of metals than the Radian Corp. (1985) data because we were sampling nearer the actual disposal zones, in most cases, than Radian did.

Using Pb as an example, it can be seen that core A (Figure 7) did not contain much metal near the surface, but increased slightly with depth similar to the B core (Figure 8). The C core (Figure 9) contained more metal at the mid-depths than at greater depths, similar to the D core (Figure 10). Although told by site managers that our E core was outside the sludge disposal area, there were high levels of metals below the 1.2 m depth in this core as well (Figure 11). In fact, the highest levels of Cu and Ni were found at about 1.25 m beneath the surface at the E site. Background (control site) levels of Pb (as well as the other metals) were within the levels typically found in soils (Figure 12). Lead levels were greatest at the surface. The Pb levels dropped sharply then increased slowly with depth.

Examining the fractionation of metals in Core A, Cd was very available in the upper 1.12 m of soil (Figure 3b). At least 80% of the Cd was in the BaCl_2 + EDTA fractions. Where Cd was present at high concentrations in the soil (≥ 1.5 m), the Cd was less available. Amorphous Fe oxides were important in Cd retention at these lower depths.

The available fraction (BaCl_2 + EDTA) of Cu in the soil was very low (Figure 4b). Copper was retained in the three oxide fractions - Mn

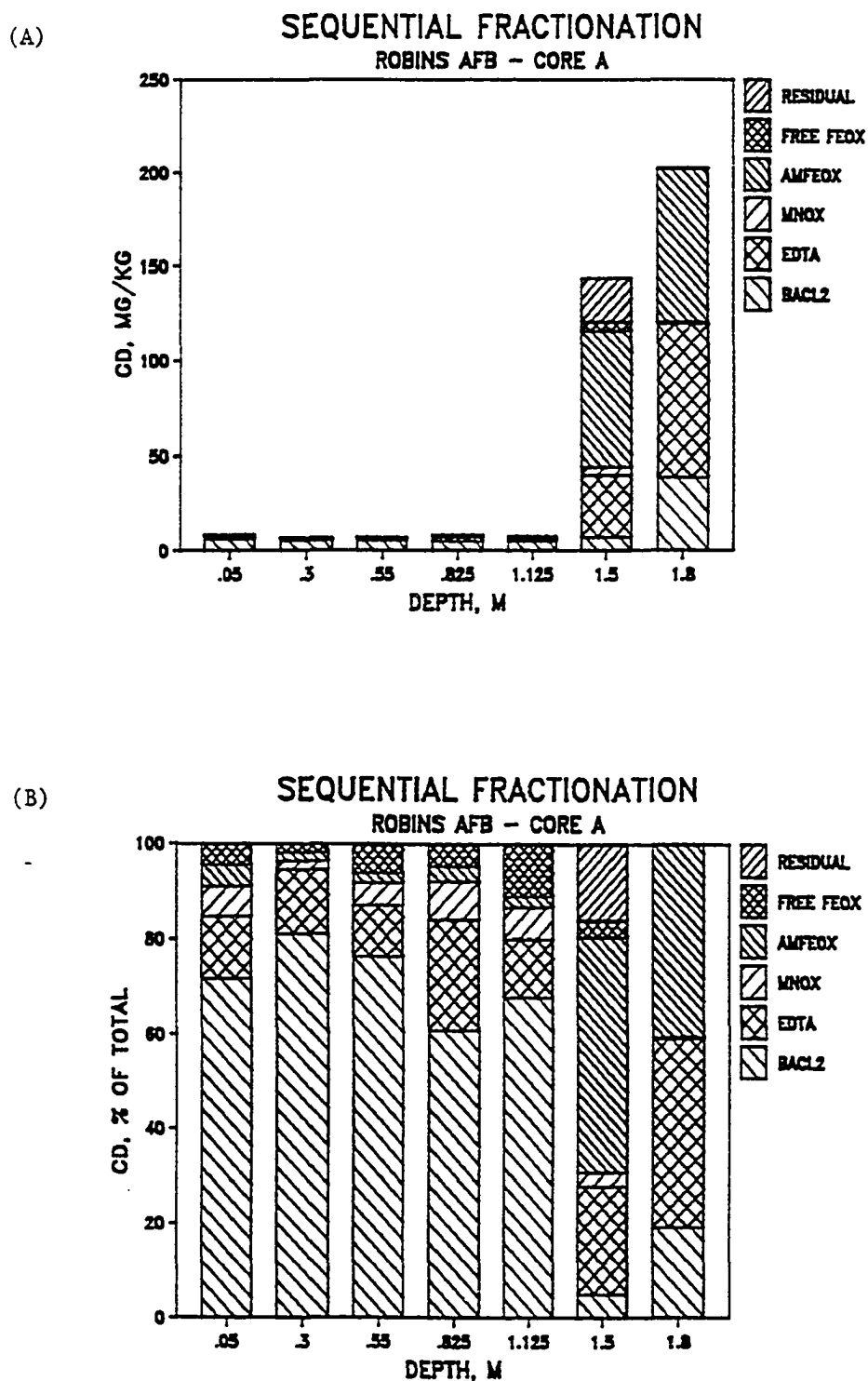
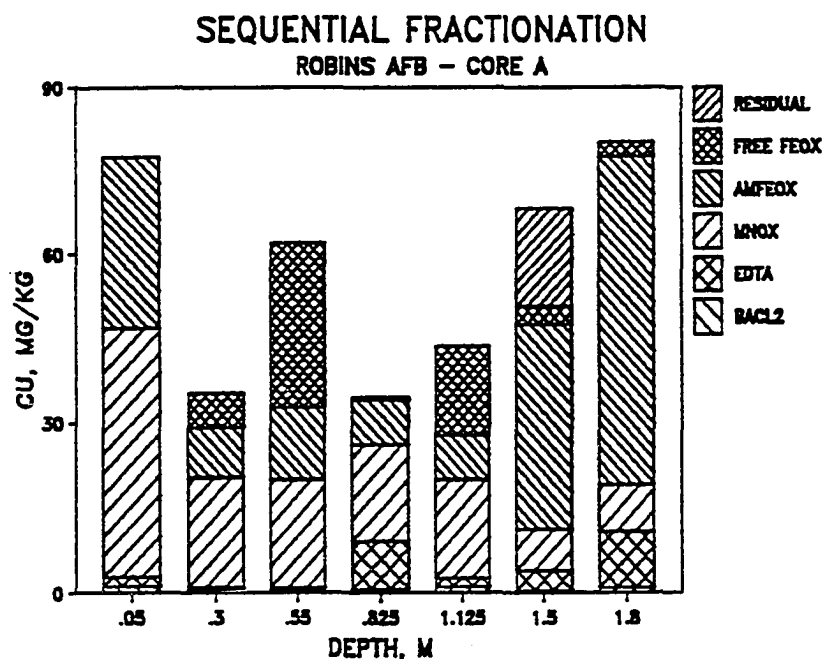


Figure 3. Distribution of Cd with depth between chemical forms in Core A at Robins AFB.

(A) Concentration

(B) Percent of total

(A)



(B)

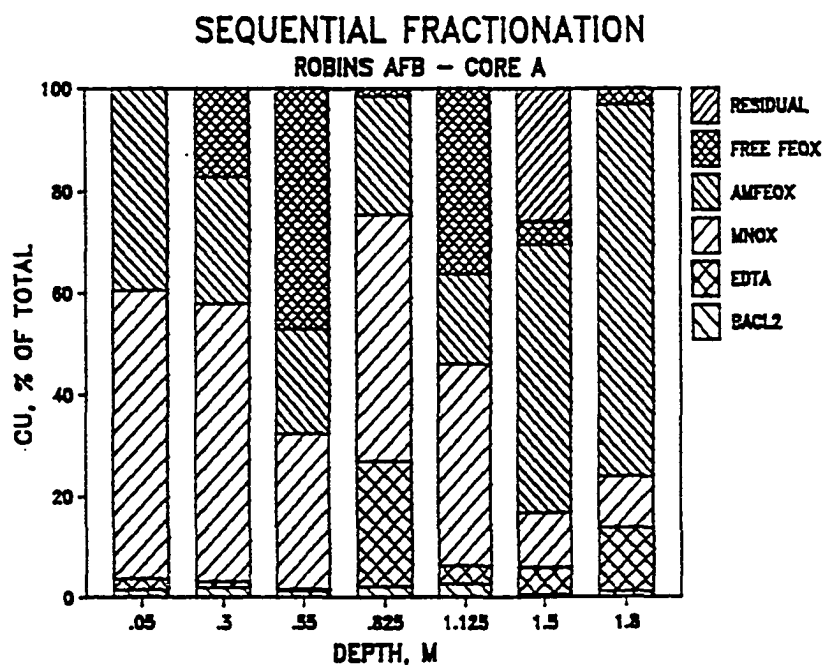
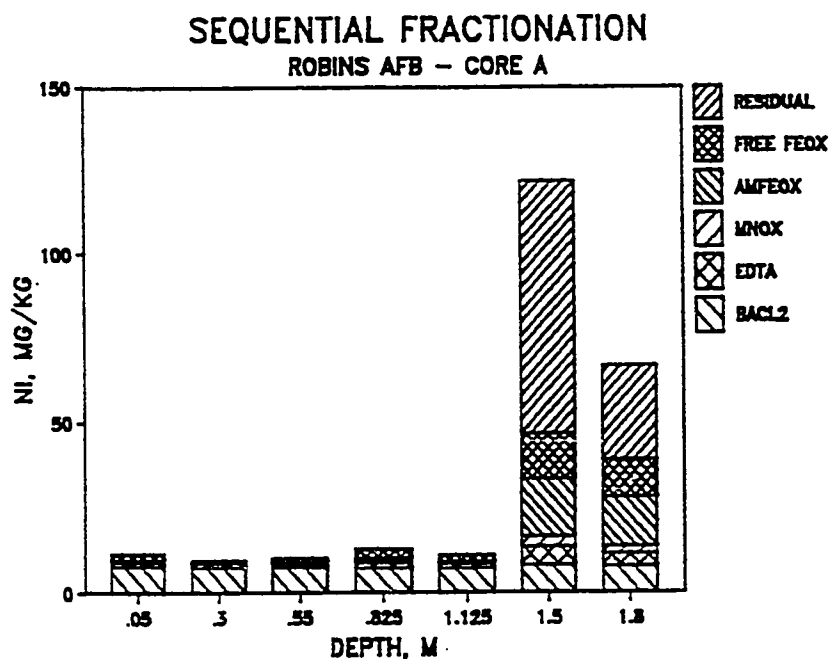


Figure 4. Distribution of Cu with depth between chemical forms in Core A at Robins AFB.

(A) Concentration

(B) Percent of total

(A)



(B)

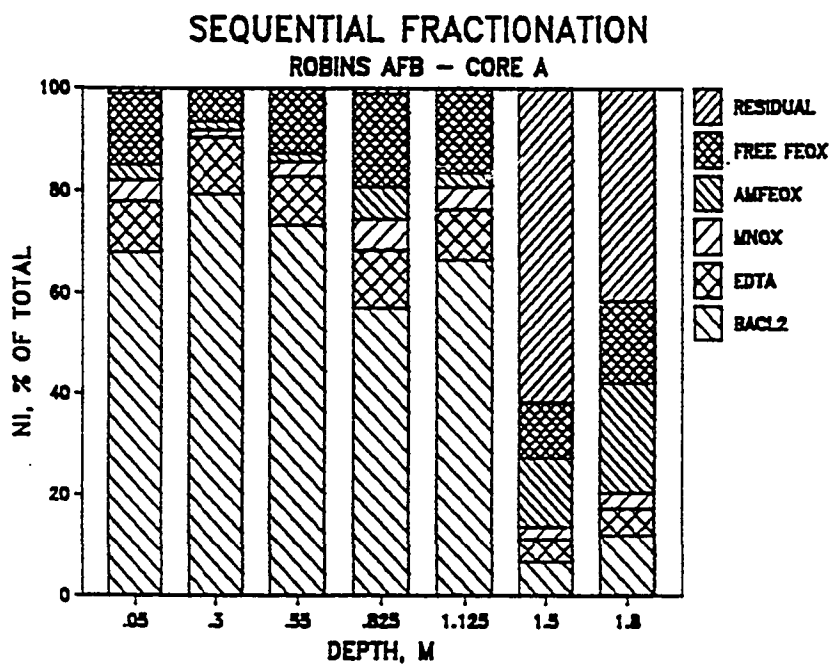
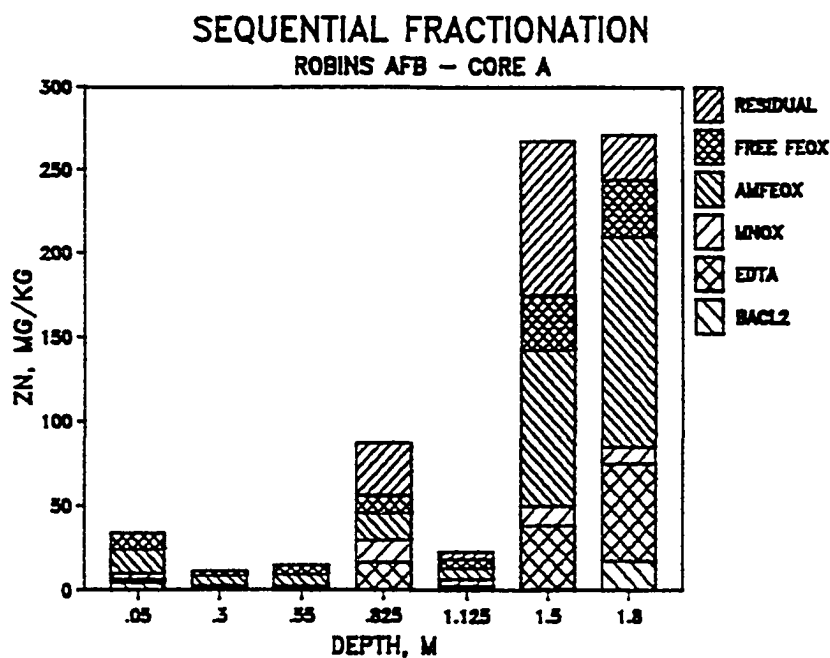


Figure 5. Distribution of Ni with depth between chemical forms in Core A at Robins AFB.

(A) Concentration

(B) Percent of total

(A)



(B)

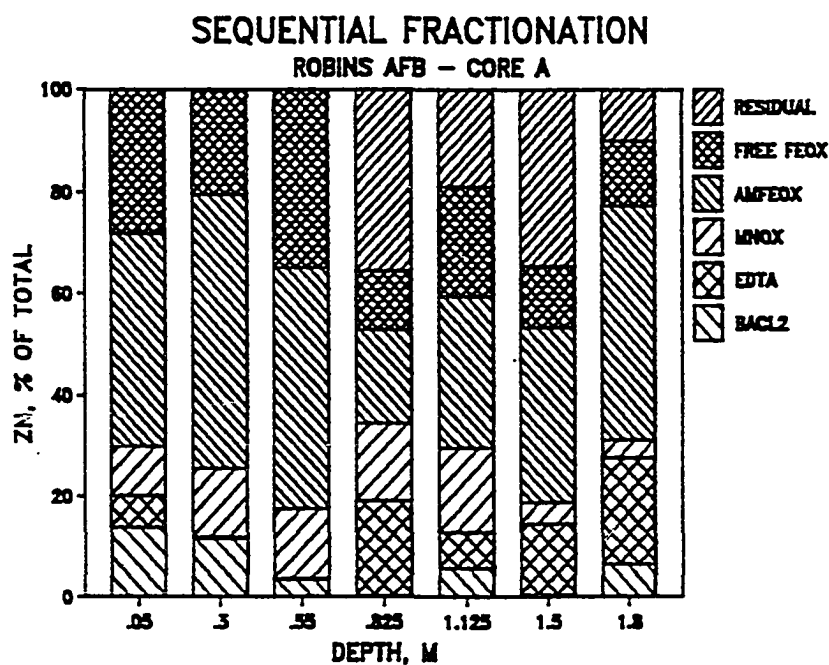
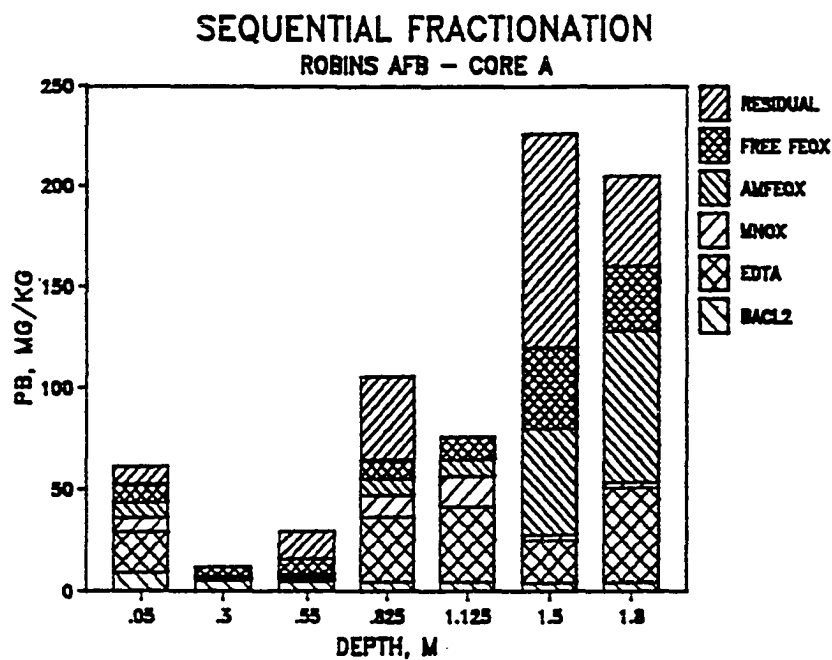


Figure 6. Distribution of Zn with depth between chemical forms in Core A at Robins AFB.

(A) Concentration

(B) Percent of total

(A)



(B)

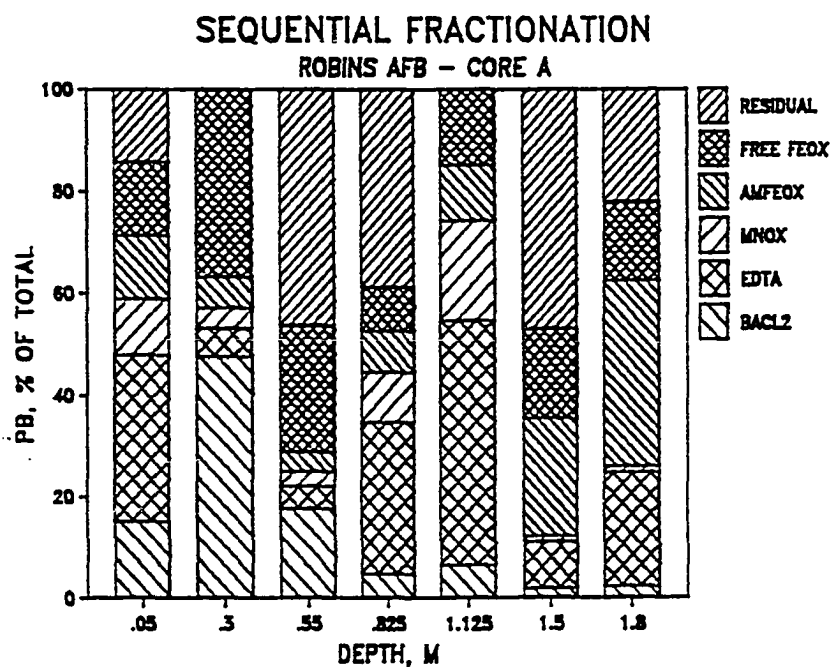
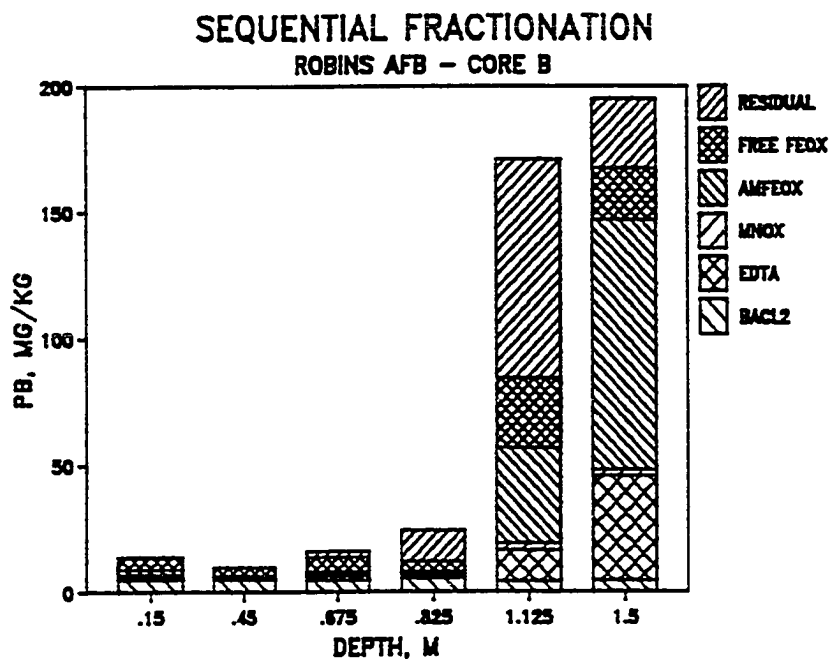


Figure 7. Distribution of Pb with depth between chemical forms in Core A at Robins AFB.

(A) Concentration

(B) Percent of total

(A)



(B)

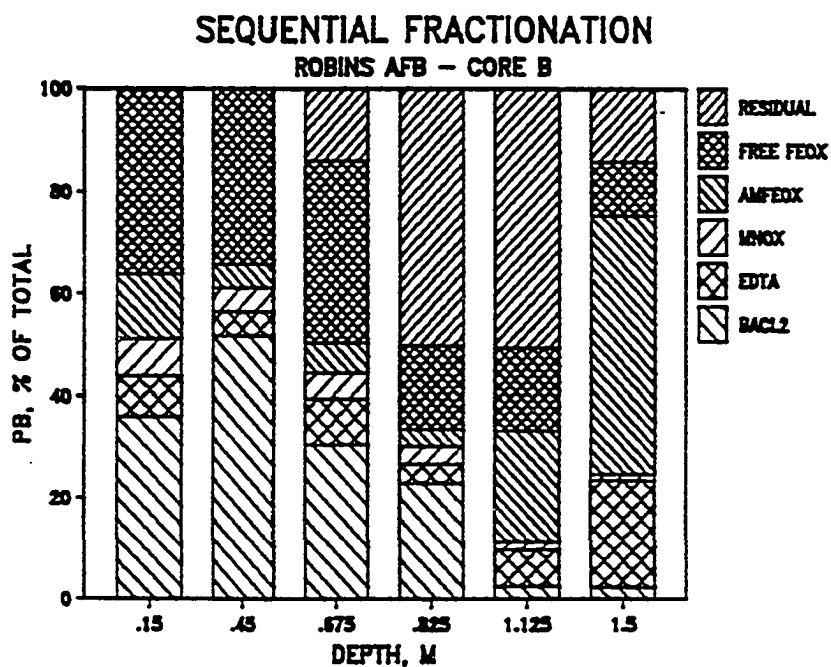
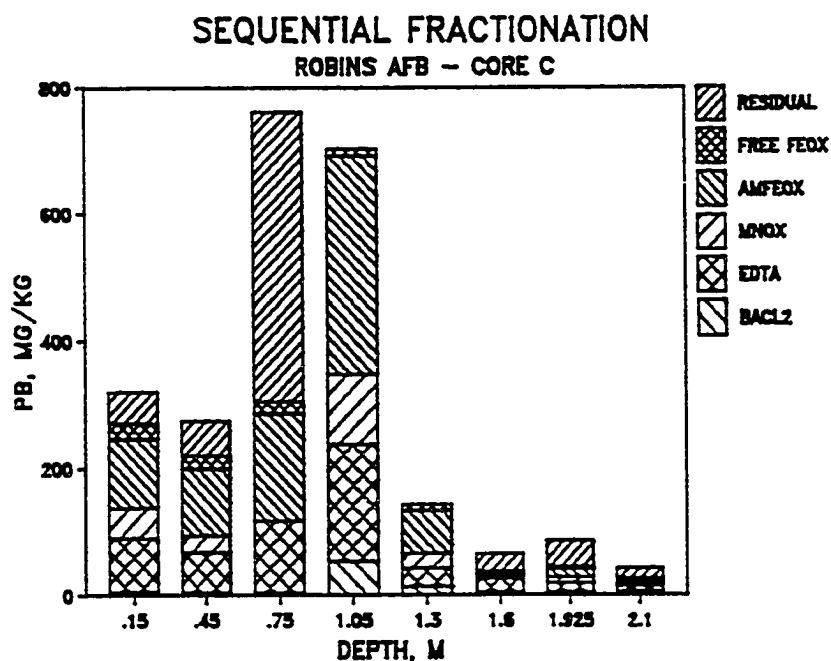


Figure 8. Distribution of Pb with depth between chemical forms in Core B at Robins AFB.

(A) Concentration

(B) Percent of total

(A)



(B)

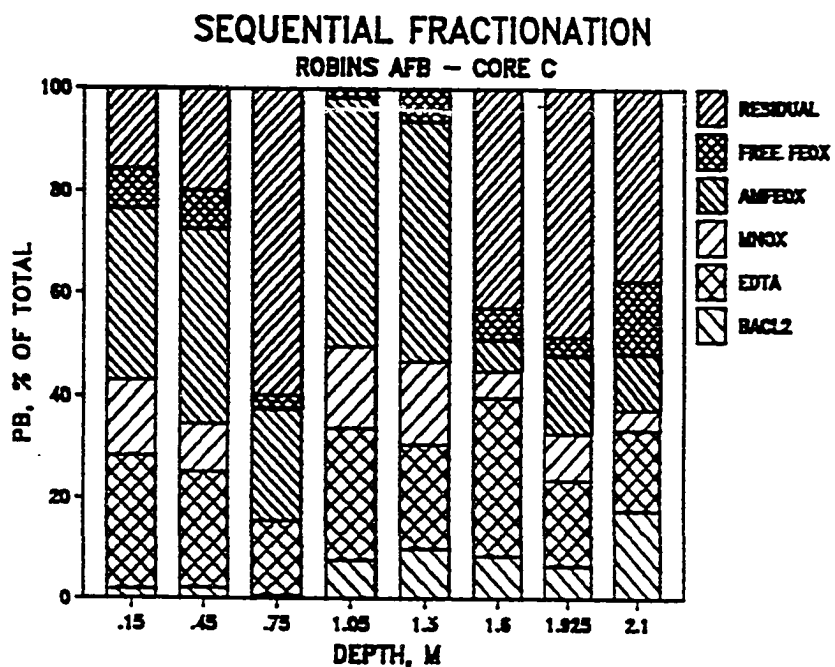
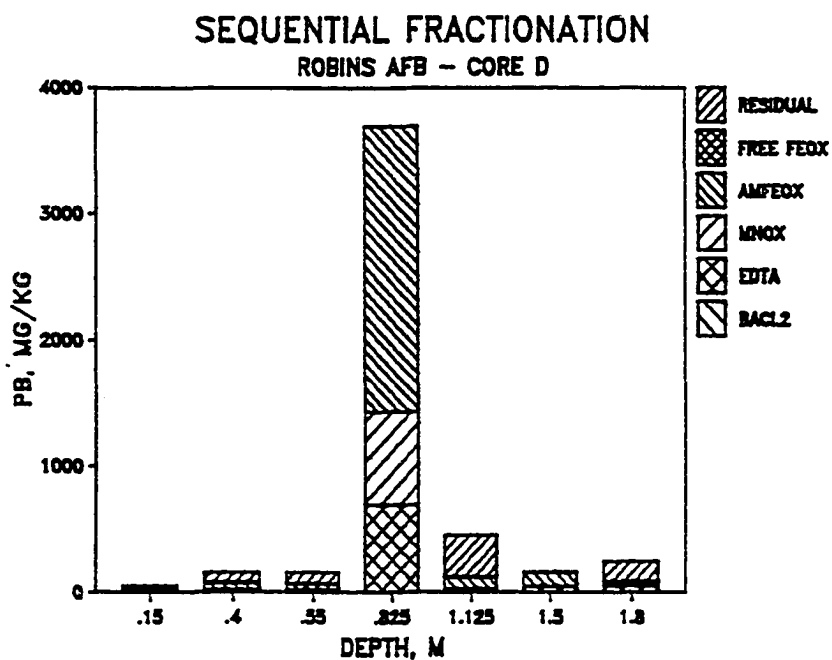


Figure 9. Distribution of Pb with depth between chemical forms in Core C at Robins AFB.

(A) Concentration

(B) Percent of total

(A)



(B)

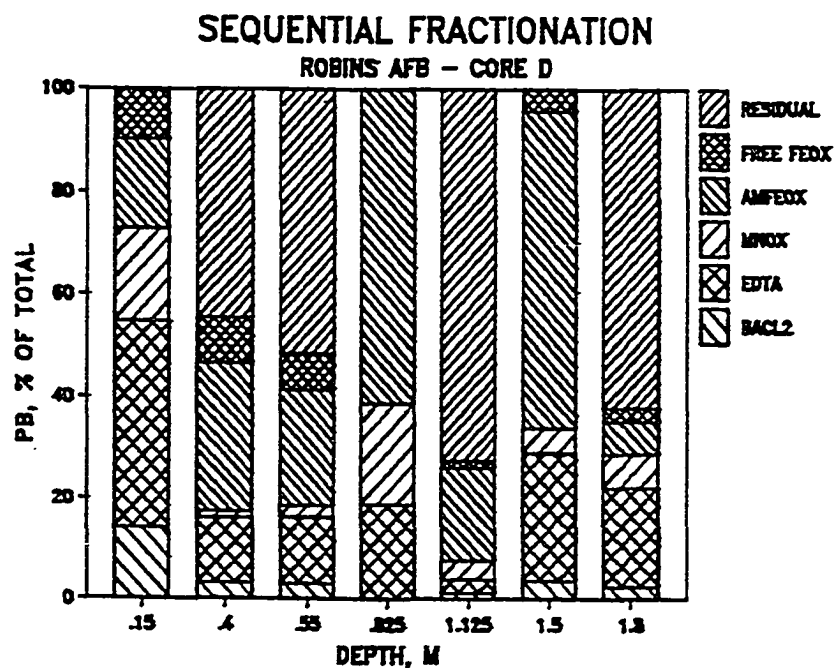
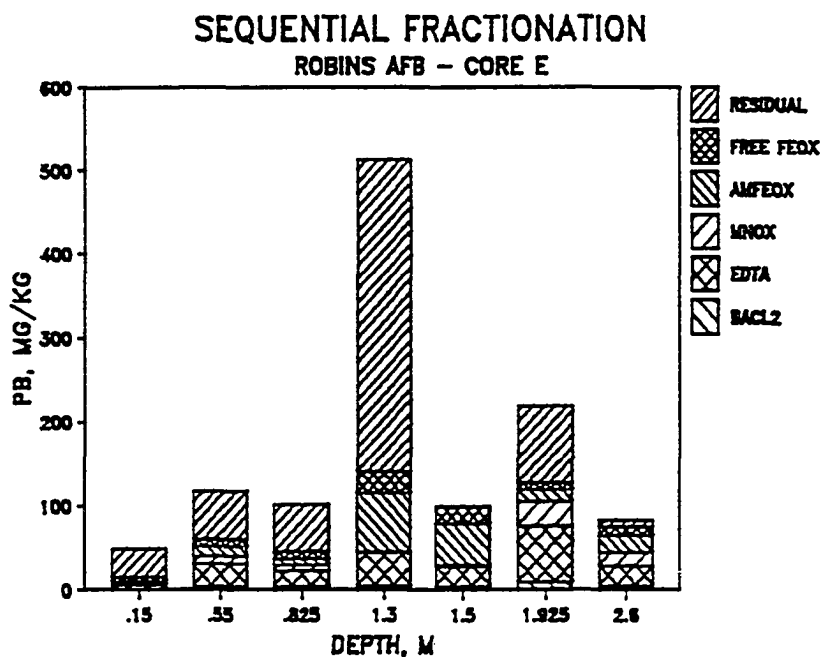


Figure 10. Distribution of Pb with depth between chemical forms in Core D at Robins AFB.

(A) Concentration

(B) Percent of total

(A)



(B)

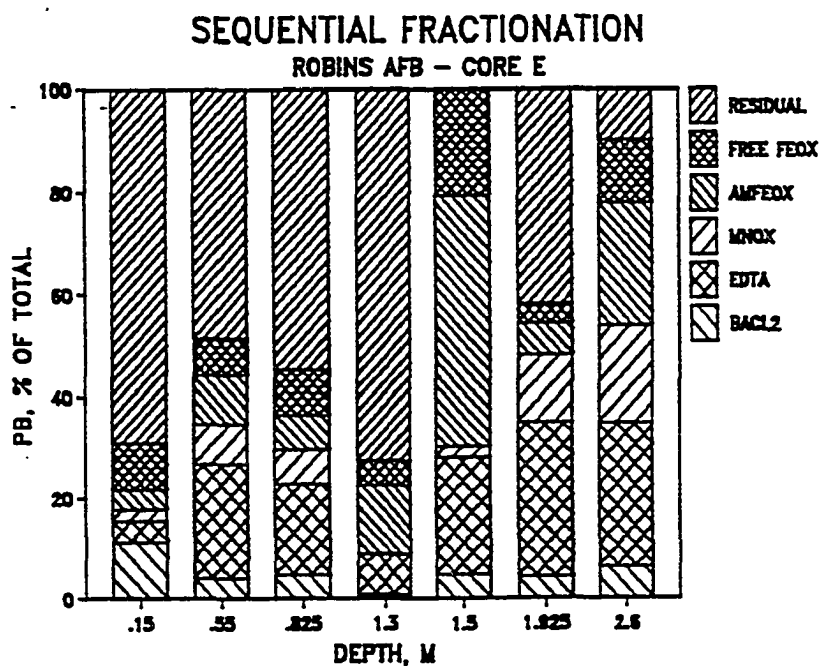


Figure 11. Distribution of Pb with depth between chemical forms in Core E at Robins AFB.

(A) Concentration

(B) Percent of total

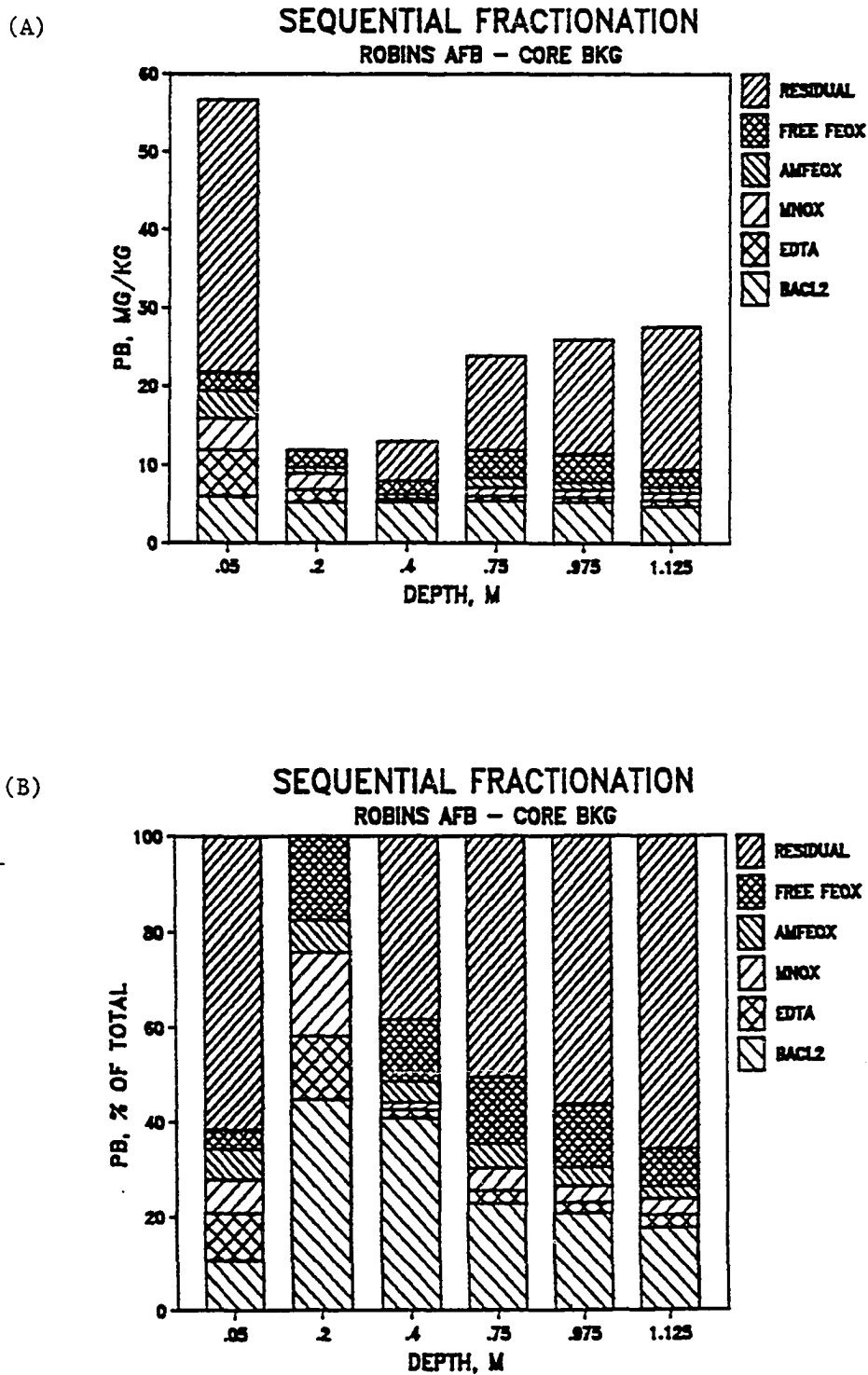


Figure 12. Distribution of Pb with depth between chemical forms in the background core at Robins AFB.

(A) Concentration

(B) Percent of total

oxide, amorphous Fe oxide, and free Fe oxide fractions. While the Mn oxide fraction appeared to predominate in the upper soil, amorphous Fe oxide predominated at the lower depths. The free Fe oxide fraction was very important at the 0.55 m and 1.12 m depths.

The fractionation of Ni (Figure 5b) was very similar to that of Cd. At least 65% of the Ni was available (BaCl_2 + EDTA fractions) in the upper 1.12 m of soil. At the lower depths, Ni was held predominately in the residual fractions. The free Fe oxide fraction, and to a lesser extent the amorphous Fe oxide fraction, were also important in Ni retention.

Less than 25% of the Zn was in available (BaCl_2 + EDTA) forms (Figure 6b). Most of the Zn was retained in the amorphous Fe oxide fraction. The free Fe oxide fraction was also very important in Zn retention.

The available fraction of Pb ranged from 10% to 50% (Figure 7b). The trend in BaCl_2 -extractable Pb was opposite total Pb - the more total Pb in the soil, the less exchangeable Pb in the soil. Typically, the EDTA fraction was greater than the BaCl_2 fraction. The three oxide fractions were important in Pb retention, and the two Fe oxide fractions, in particular. The residual fraction was also very important at certain depths.

The fractionation of the metals varied from core to core. However, the overall trends were the same. Lead was more available where the total concentration of Pb was lower; the two Fe oxide fractions and the residual fraction were important in Pb retention (Figures 8-12).

Long-Term Release of Metals

Cadmium was released from some of the soil samples over time (Figure 13), especially from the E core. Up to $14 \text{ mg} \cdot \text{L}^{-1}$ was released from the

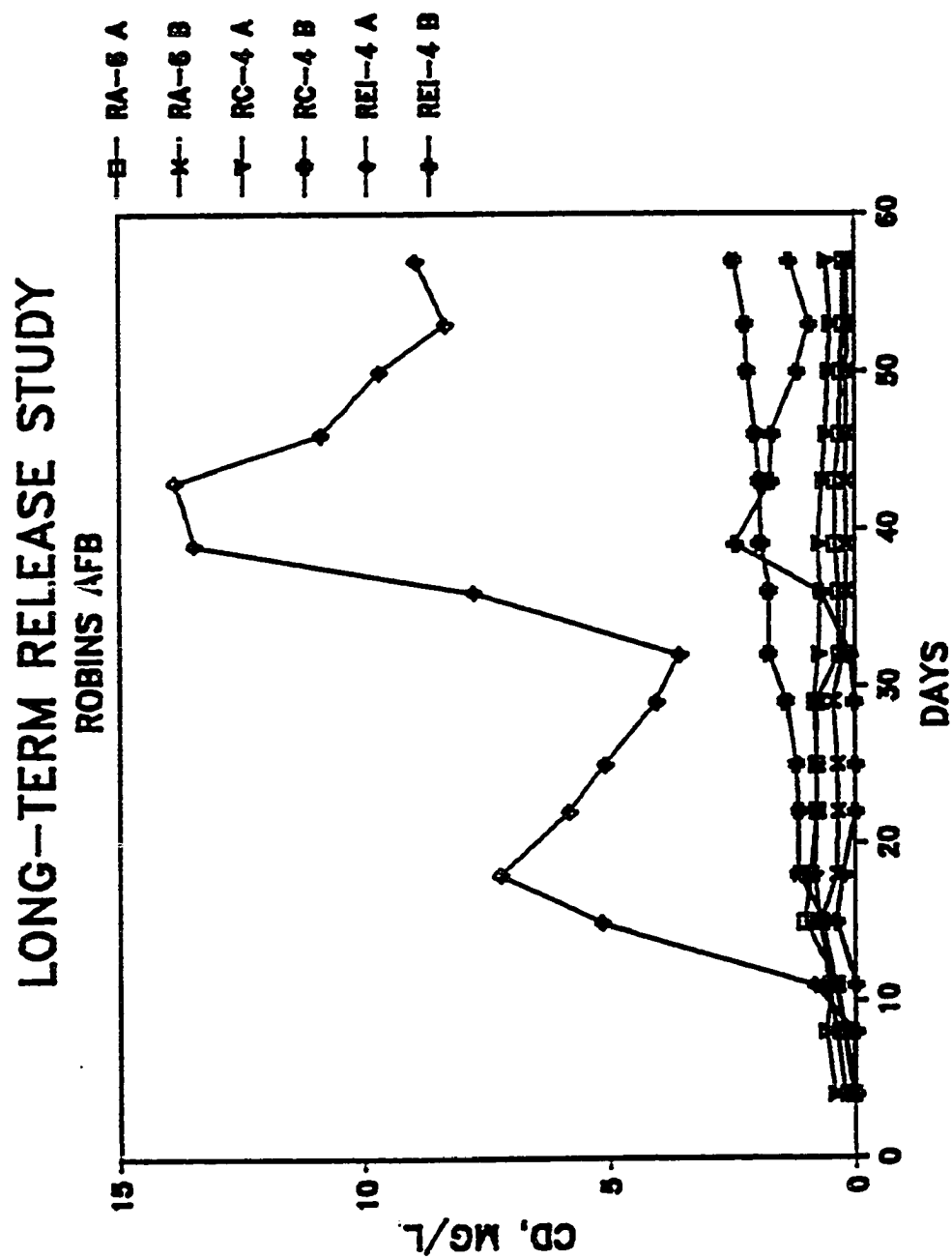


Figure 13. Release of Cd over time from selected contaminated soil samples from Robins AFB.

RE1-4 A sample. It appeared that Cd was released under oxidizing conditions and readsorbed under reducing conditions in this E core material.

Very low levels of Cu were detected in solution at any time, with more Cu released under reducing conditions (Figure 14). A spike in Cu concentration in most of the samples occurred at Day 28, corresponding to a spike in Pb, Zn, and Fe concentrations.

Very low levels of Ni were also detected in solution at any time (Figure 15). Some samples released Ni over time, while other samples readsorbed the initially released Ni, particularly the Core A samples.

Lead was released over time from the RC-4 B sample but not from the other samples (Figure 16). A spike in Pb concentration occurred at Day 28, as was noted earlier.

Zinc was released over time from the soil samples (Figure 17), with the most released from sample RC-4 A. A spike occurred in Zn concentration in some of the samples at Day 28, as was noted earlier.

More Fe was released under reducing conditions than under oxidizing conditions (Figure 18). A spike occurred in Fe concentration at Day 28, as was noted earlier, and then again at Day 44.

Solution concentration of Mn over time varied, depending on the sample (Figure 19). It either remained steady (RC-4), increased (RE1-4), or increased during the first two weeks then decreased (RA-6).

Because the system was not well poised, the measured Eh values fluctuated greatly between readings. Therefore, the data is not presented. It is assumed, however, that the purging gases did have an effect on the oxygen status and thus the metal chemistry of the soil suspension, as discussed above.

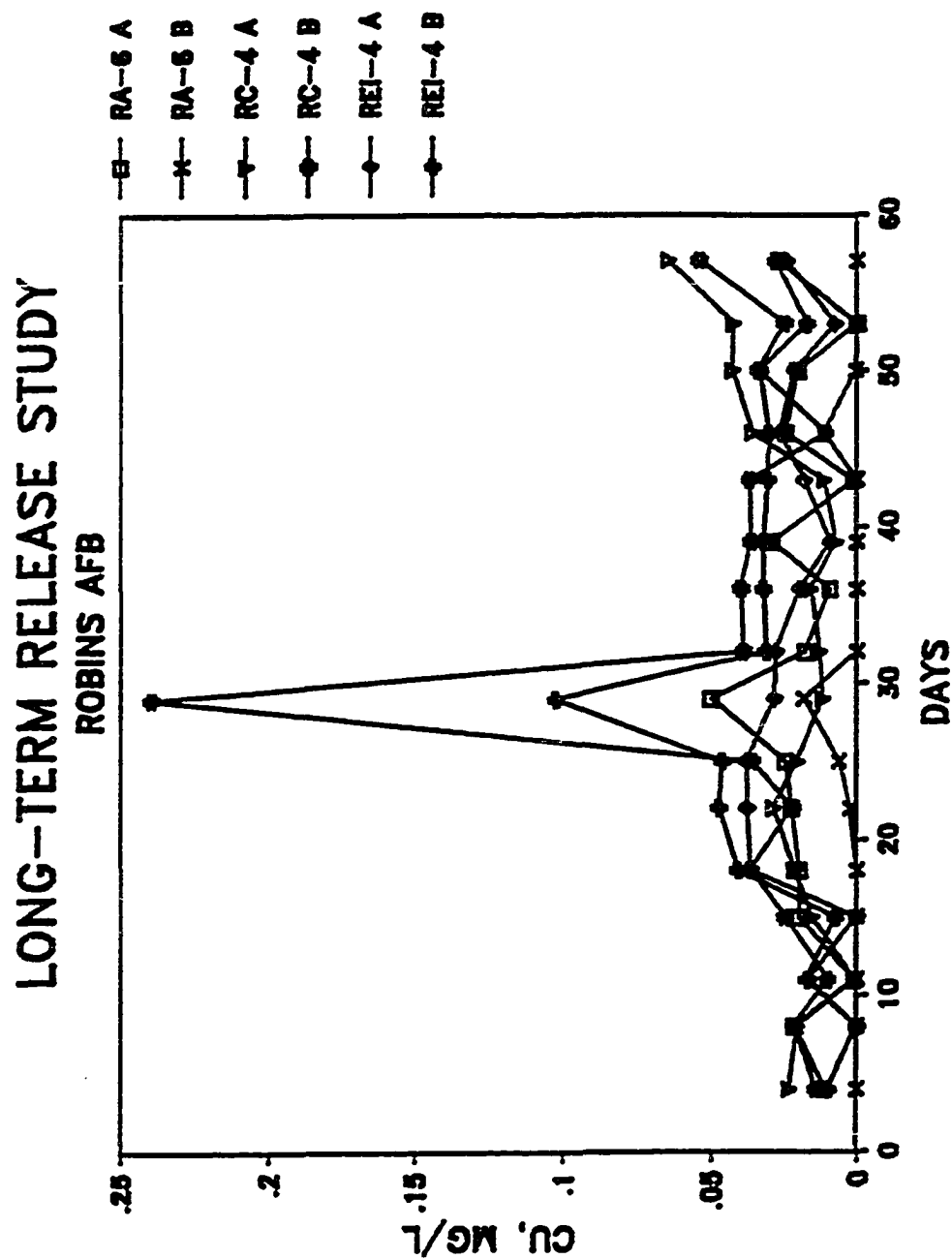


Figure 14. Release of Cu over time from selected contaminated soil samples from Robins AFB.

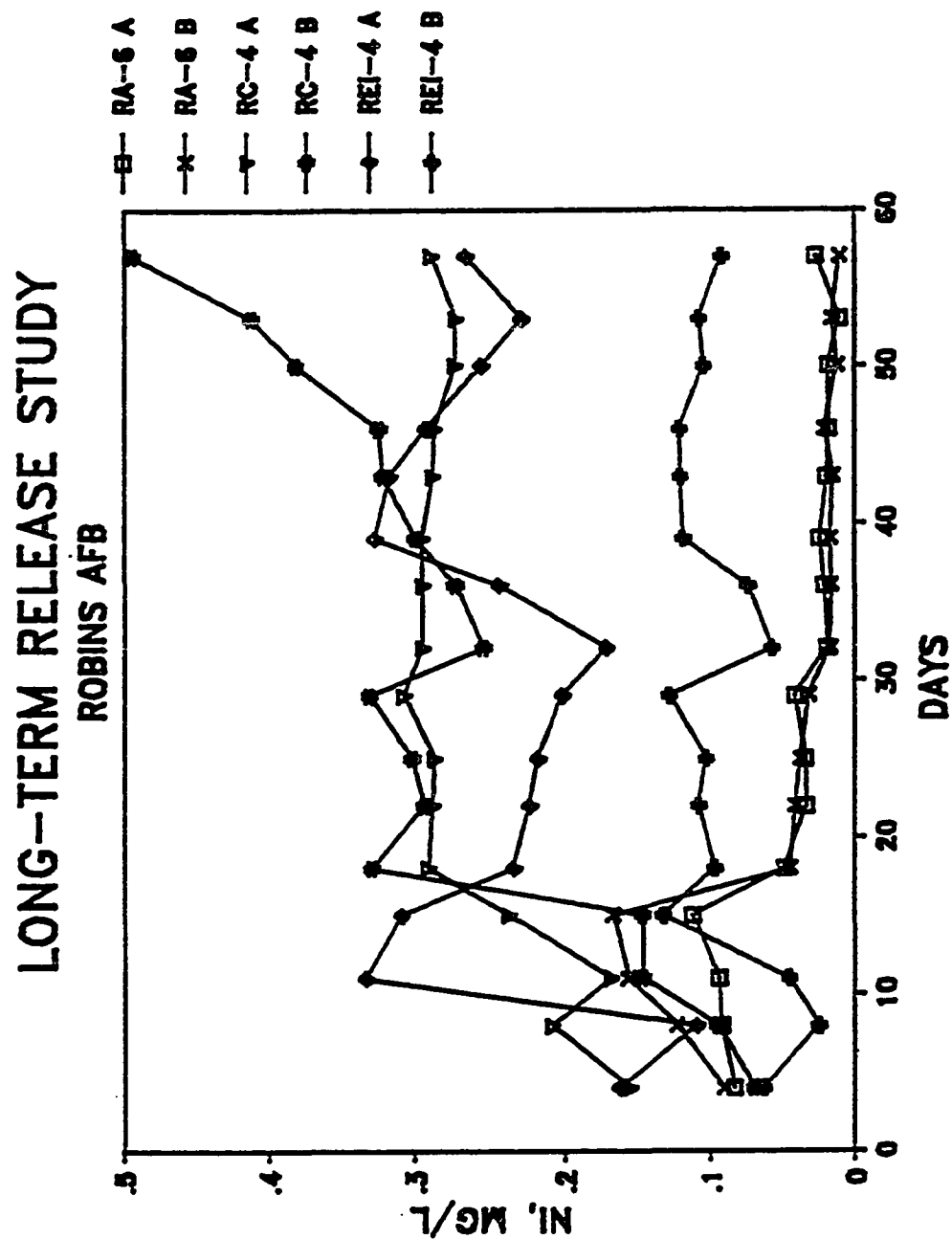


Figure 15. Release of Ni over time from selected contaminated soil samples from Robins AFB.

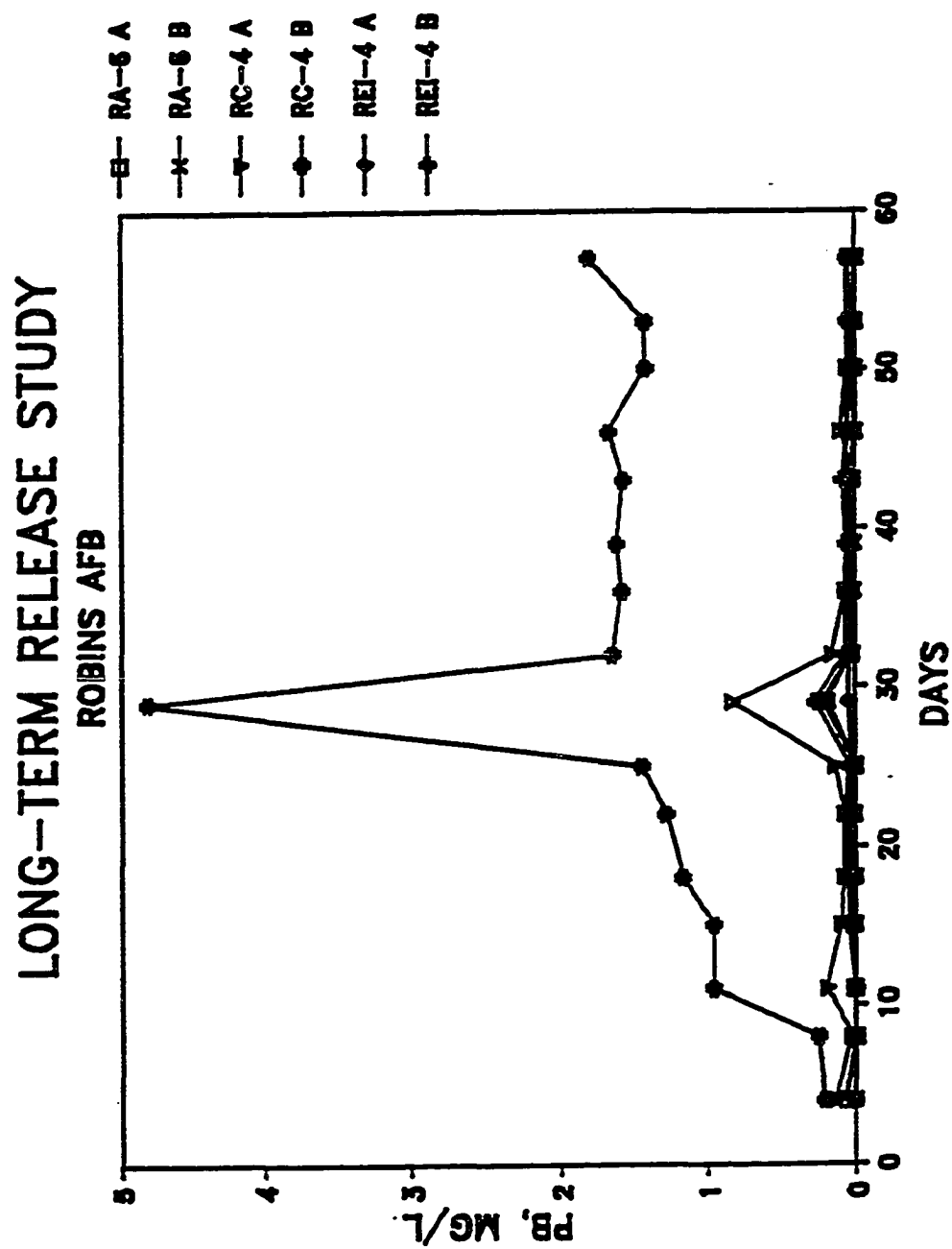


Figure 16. Release of Pb over time from selected contaminated soil samples from Robins AFB.

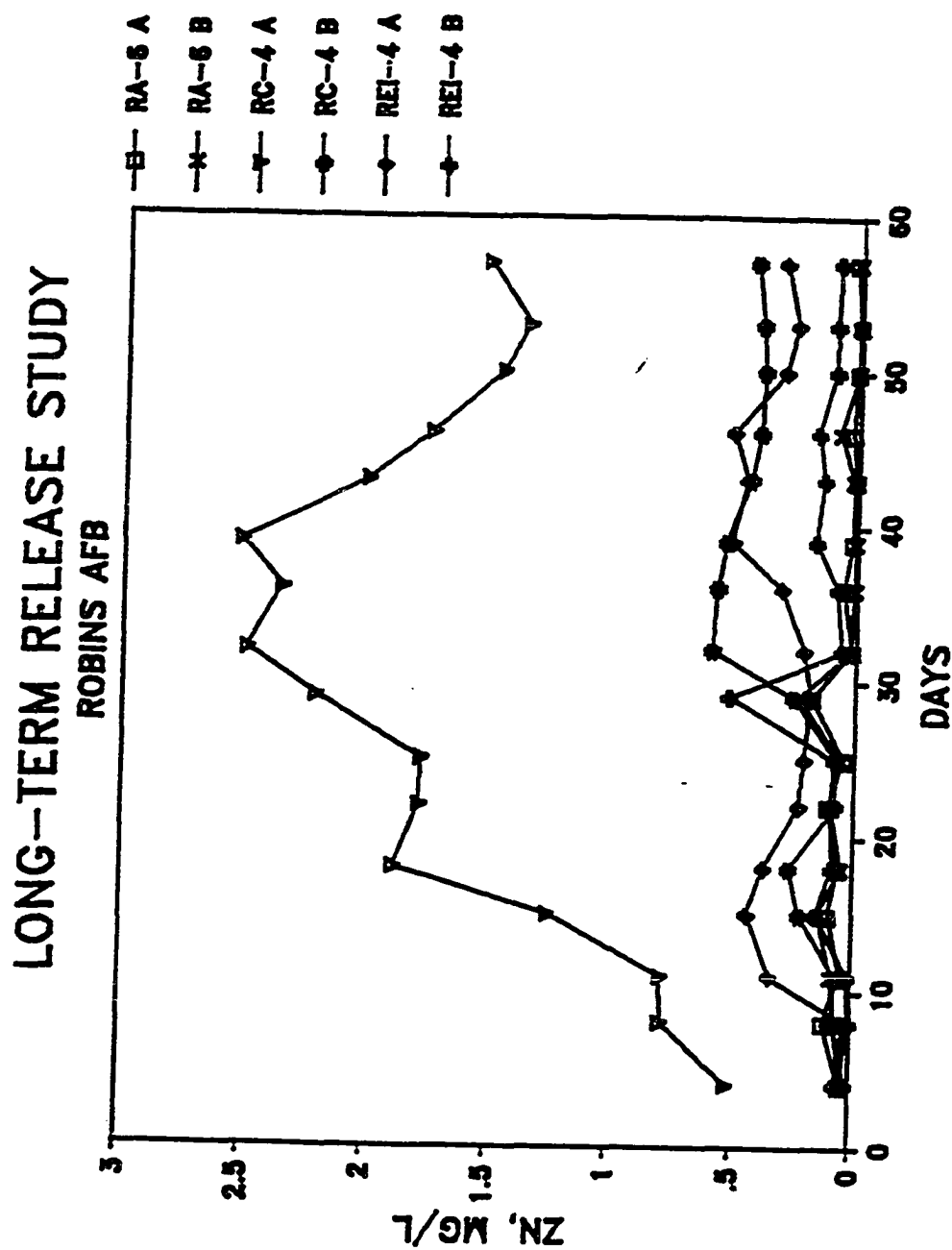


Figure 17. Release of Zn over time from selected contaminated soil samples from Robins AFB.

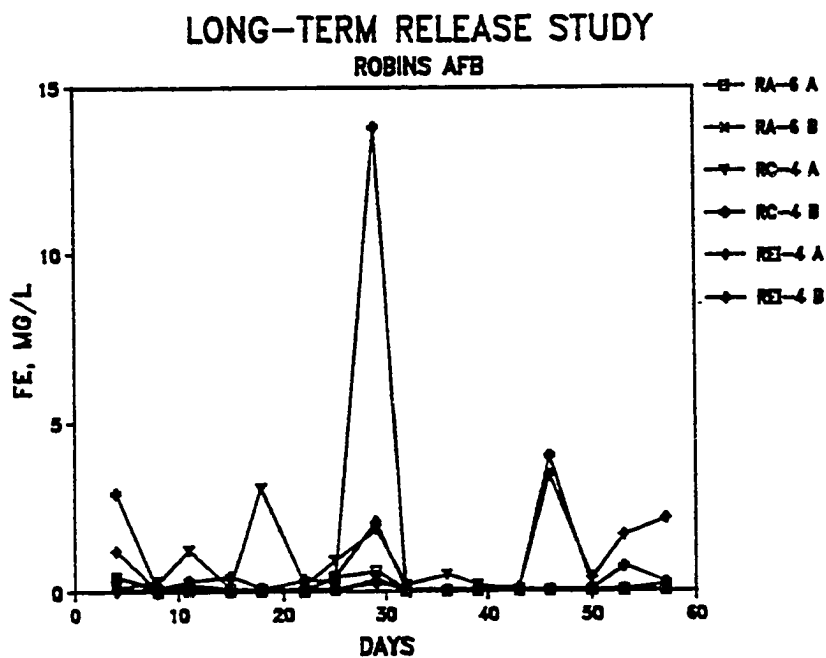


Figure 18. Release of Fe over time from selected contaminated soil samples from Robins AFB.

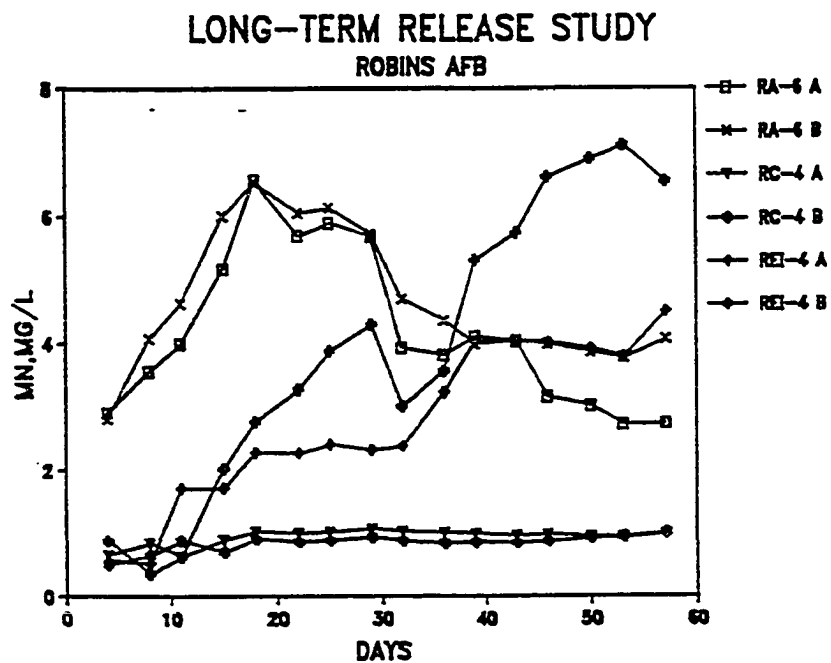


Figure 19. Release of Mn over time from selected contaminated soil samples from Robins AFB.

DISCUSSION

Chemical Forms

The levels of the different metals in Core A typically followed the same trends with depth, except Cu was higher in some samples than were the other metals. Considering the low swampy elevation and the oily liquids present, it is possible that winter floods and high water caused the "oil" and some associated metals to move from the deeper depths, where they were originally deposited, to the more shallow depths. The highest levels of the metals were associated with a black, oily substance in the soil, presumably a part of the industrial waste disposed of in the lagoon. Metal levels were not high in all samples containing the oily substance, however. Metals were associated with the oily substance in Core E, indicating that metals were migrating with the oily substance out of the disposal zone. This assumes that information provided that Core E was outside the disposal area was accurate.

The fractionation of Cd and Ni were similar. The readily available forms predominated where the metals were present at lower concentrations. It is possible that these metals, being relatively mobile but depleted in the upper core, have migrated down to the lower depths to be retained by the oxides - amorphous Fe oxide for Cd and free Fe oxides and amorphous Fe oxides for Ni. Exchangeable Pb also showed these same trends as for Cd and Ni - being greater where total Pb was least. Again, the Pb may be migrating to deeper depths to be retained by the oxides. However, it is more likely that the metals were deposited at these levels.

Cadmium retention was predominately by the amorphous Fe oxide fraction. The three oxide fractions were important in Cu and Pb

retention. The residual fraction was also important in Pb retention at some depths. The residual fraction was most important in Ni retention, followed by the free Fe oxide fraction then the amorphous Fe oxide fraction. The amorphous Fe oxide fraction was most important in Zn retention, followed by the free Fe oxide fraction. These results are in agreement with those reported in the literature. Khalid et al. (1978) reported that Cu, Zn, and Pb were retained by hydrous oxides of Fe and possibly Mn in the sediments. Nair and Cottenie (1971) concluded that there was convincing statistical proof that amorphous Fe oxides retained a large portion of the Cu, Pb, and Zn in their investigations.

The fractionation of the metals varied greatly with depth. Because the waste was deposited at the site over a long time, the waste varied greatly with depth. Thus, the variability of the waste with depth probably caused the variability in the chemical forms of the metals. Therefore, it can be concluded that the waste greatly affect metal chemistry at this site.

Long-Term Release of Metals

It appeared that Cd was released under oxidizing conditions and often readsorbed under reducing conditions. Khalid et al. (1979, 1981) reported that the recovery of ^{109}Cd in soluble and exchangeable forms was negligible under reduced conditions (-150 mV and 0 mV). The researchers found a marked increase in ^{109}Cd solution concentrations as the reduced suspensions were oxidized.

The release of Cu, Pb, and Zn resembled the release of Fe, indicating that at least some of the Cu, Pb, and Zn were adsorbed by or

coprecipitated with Fe oxide. When the Fe oxides were reduced to soluble Fe, the metals were released.

The release of Cd and Ni may be related to the release of Mn when Mn oxide is reduced. The agreement between Cd and Ni and Mn release was not as good as for Cu, Pb, and Zn with Fe release.

The results of this study agree with the chemical fractionation work, showing the importance of the metal oxides in the retention of metals by the soil.

SUMMARY AND CONCLUSIONS

Levels of Cd, Cu, Pb, and Zn in soil samples from Robins AFB were above those typically found in soils and were believed to be associated with the industrial wastes disposed of at this site. Of the more than 25 samples obtained from the disposal site cores plus E core (adjacent to the industrial sludge disposal site), eight contained about $100 \text{ mg}\cdot\text{kg}^{-1}$ or higher levels of Cd (Cd ranged to more than $900 \text{ mg}\cdot\text{kg}^{-1}$), six contained about $100 \text{ mg}\cdot\text{kg}^{-1}$ or higher levels of Cu (Cu ranged to $550 \text{ mg}\cdot\text{kg}^{-1}$), four contained more than $100 \text{ mg}\cdot\text{kg}^{-1}$ Ni (Ni ranged to near $250 \text{ mg}\cdot\text{kg}^{-1}$), 14 contained about $200 \text{ mg}\cdot\text{kg}^{-1}$ or higher levels of Pb (Pb ranged to more than $2700 \text{ mg}\cdot\text{kg}^{-1}$), and 13 contained about $200 \text{ mg}\cdot\text{kg}^{-1}$ or higher levels of Zn (Zn ranged to more than $1400 \text{ mg}\cdot\text{kg}^{-1}$).

Cadmium retention was predominately by the amorphous Fe oxide fraction. The three oxide fractions were important in Cu and Pb retention. The residual fraction was also important in Pb retention at some depths. The residual fraction was most important in Ni retention, followed by the free Fe oxide fraction then the amorphous Fe oxide

fraction. The amorphous Fe oxide fraction was most important in Zn retention, followed by the free Fe oxide fraction.

The samples obtained from Robins AFB were highly contaminated with what we were told was a mixture of hazardous organics. It should be emphasized that the core from an adjacent area between the sludge disposal pit and the surrounding swamp (E core) was also saturated with the same oily liquid as the pit samples, and also contained some of the highest metal levels. If information provided us that our Core E samples were taken out of the sludge disposal area is correct, then the data indicate movement of high concentrations of several metals has occurred in the shallow groundwater at this location. Clearly, this is a site with a high potential for metals movement through subsoils. This movement was likely facilitated by sandy soils and/or high levels of organic and other wastes present.

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CHAPTER 5

THE EFFECT OF SOIL PROPERTIES AND SOLUTION COMPOSITION
ON CADMIUM AND LEAD RETENTION BY SUBSOILS

ABSTRACT

The mobility of metals in soils is dependent upon the soil's physical and chemical properties and the composition of the solution with which the metals are associated. Batch equilibrium metal retention studies were conducted with five subsoil materials and four synthetic waste solutions and a simulate soil solution (control) containing varying concentrations of Pb and Cd to determined the effects of soil properties and solution composition on Cd and Pb retention. The Freundlich parameter, Log K, for both Cd and Pb was correlated with pH, CEC, and percent silt, and negatively correlated with percent sand. The composition of the solution containing the metals influenced Cd and Pb retention by soil. For Cd, retention followed the order: $0.005M \text{ Ca(NO}_3)_2$ + Cd only \geq oil field waste $>$ $0.005M \text{ Ca(NO}_3)_2$ + Cd+Pb $>$ synthetic leachate \geq acidic metals waste. For Pb, the order was $0.005M \text{ Ca(NO}_3)_2$ + Pb only \geq oil field waste \geq $0.005M \text{ Ca(NO}_3)_2$ + Pb+Cd $>$ acidic metals waste \geq synthetic leachate.

INTRODUCTION

The degree of metal immobilization or transport in soils depends upon an interaction between soil properties, amount of metals present, and the properties of the leachate phase with which the metals are associated. Soil properties affecting metal mobility include bulk density, surface area, particle-size distribution, pH, redox status, ion exchange capacity, amount of organic matter, type and amount of metal oxides, and type and amount of clay minerals (Amacher et al., 1986). There are a number of reviews and reports on factors affecting the mobility and plant availability of trace and toxic metals. Much of this work has focused on topsoils or sediments containing an appreciable amount of naturally occurring organic matter compared to subsoils. Soil humic material is known to be very effective in immobilizing most trace and toxic metals. Since subsoils contain much less organic matter and are the primary transport media if metals contamination of groundwater is to occur, research efforts should be directed toward processes regulating metal mobility in subsoils.

Solution composition will also greatly affect metal retention and movement. LaBauve et al. (1988), Benjamin and Leckie (1982), Garcia-Miragaya and Page (1976), and Knox and Jones (1979) reported that complexation of Cd reduced Cd retention by soils. LaBauve et al. (1988) and Brown (1979) stated that formation of Pb complexes decreased Pb retention by soils.

The Freundlich equation has often been used to describe metal retention by soils:

$$S = K_D C^n \quad (1)$$

where S is the amount of metal retained per unit mass of soil, C is the equilibrium concentration of the element of interest, and K_D and n are empirical coefficients.

The Freundlich equation has been found to correspond to an adsorption model in which the affinity of the adsorption sites decreases exponentially as adsorption increases (Soon, 1981). Garcia-Miragaya and Page (1976) postulated that the coefficient, K , is a good index of the relative Cd retention affinities of various soils.

The objective of this study was to demonstrate the interaction between soil properties and waste solutions on the movement of metals in subsoils.

MATERIALS AND METHODS

Soil Selection and Characterization

Five subsoil materials of different physical and chemical properties were selected for this study to determine the effect of the soils' physical and chemical properties on Cd and Pb retention. The sampling location and classification of the soil materials are presented in Table 1, and selected soil properties are listed in Table 2. The pH of the samples was determined in a 1:1 soil:water paste (McLean, 1982). Cation exchange capacity (CEC) was determined by summing the major cations (Ca, Mg, Na, K, and Al) extracted with 0.1M BaCl₂ (adapted from Rhoades, 1982). Particle-size distribution was determined by the hydrometer method (Gee

Table 1. Classification of soil materials used in study.

Designation	Soil Series	Taxonomic Classification
Cecil	Cecil	clayey, kaolinitic, thermic, Typic Hapludult
Combustion	unknown	
Pontchatoula	unknown	
Robins AFB	Norfolk	fine-loamy, siliceous, thermic, Typic Paleudult
Tinker	Vernon	fine, mixed, thermic, Typic Ustochrepts

Table 2. Selected chemical and physical properties of soils used in study.

Soil	pH	CEC	MnO ₂	Amorph. Total		Sand	Silt	Clay
				Fe ₂ O ₃	Fe ₂ O ₃			
		cmol(+)/kg		-----	%	-----		
<hr/>								
Cecil	4.92	2.58	0.005	0.051	1.030	18	9	73
Combustion	7.00	10.37	0.071	0.141	0.213	17	54	29
Pontchatoula	6.49	15.33	0.005	0.034	0.092	27	36	37
Robins AFB	3.50	1.31	0.001	0.014	0.059	72	13	15
Tinker AFB	7.60	28.94	0.015	0.034	0.291	0	45	55

and Bauder, 1986). The Mn oxide content of the samples was extracted using pH 2, 0.1M hydroxylamine hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$) (Chao, 1972). Amorphous Fe oxides were determined using 0.25M hydroxylamine hydrochloride-0.25M HCl (Chao and Zhou, 1983). Free Fe oxides were determined using the dithionite-citrate-bicarbonate (DCB) method (Mehra and Jackson, 1960).

Experimental Procedure

The subsoil material was air-dried and ground to pass a 2-mm sieve prior to use. To determine the effect of wastes on Cd and Pb retention, four waste solutions were used (Table 3). The concentrations of Cd and Pb used in conjunction with the four waste solutions ranged from 1 $\text{mg}\cdot\text{L}^{-1}$ Cd + 10 $\text{mg}\cdot\text{L}^{-1}$ Pb to 50 $\text{mg}\cdot\text{L}^{-1}$ Cd + 500 $\text{mg}\cdot\text{L}^{-1}$ Pb. A fifth and sixth waste solution contained 1 $\text{mg}\cdot\text{L}^{-1}$ Cd to 50 $\text{mg}\cdot\text{L}^{-1}$ Cd and 10 $\text{mg}\cdot\text{L}^{-1}$ Pb to 500 $\text{mg}\cdot\text{L}^{-1}$ Pb, respectively.

To duplicate 50-mL centrifuge tubes, 4 g of soil and 20 mL of simulated waste-metal solution were added. The samples were shaken for 24 hr on a reciprocating shaker at 140 $\text{osc}\cdot\text{min}^{-1}$, then filtered through a #40 Whatman filter. The solution phase was analyzed for metals on an inductively coupled argon plasma emission spectrometer (ICP).

Calculation of Adsorption Coefficients

The Freundlich isotherm, in its linear form, is:

$$\log(S) = \log(K_D) + n\log(C) \quad (1)$$

where S is the amount of metal retained, $\text{mg}\cdot\text{kg}^{-1}$, C is the equilibrium metal concentration in solution, $\text{mg}\cdot\text{L}^{-1}$, log K is the intercept of the Freundlich isotherm, and n is the slope of the Freundlich isotherm. The

Table 3. Composition of synthetic waste solutions used in study.

Waste Solution	Composition
$\text{Ca}(\text{NO}_3)_2^{\dagger}$	0.005M $\text{Ca}(\text{NO}_3)_2$
Synthetic Municipal Landfill	0.15M sodium acetate
Leachate (Aerobic) [‡]	0.15M acetic acid
	0.050M glycine
	0.007M salicylic acid
Acidic Metals Waste	100 mg•L ⁻¹ Cu
	200 mg•L ⁻¹ Cr
	200 mg•L ⁻¹ Ni
	300 mg•L ⁻¹ Zn
	HCl to pH 2
Oil Field Waste [§]	25 mg•L ⁻¹ naphthalene
	50 mg•L ⁻¹ Ba
	10 mg•L ⁻¹ Cr(III)

[†]Amacher et al., 1986.

[‡]Stanforth et al., 1979.

[§]Pardue (unpubl.).

Freundlich parameters, $\log K_D$ and n , can be obtained by plotting $\log S$ versus $\log C$, with n being the slope and $\log K_D$ the intercept of the line.

RESULTS AND DISCUSSION

Effect of Soil Properties on Metal Retention

The effect of soil properties on Cd and Pb retention was determined using five subsoil materials. The amount of metal retained by the soil was plotted on a log-log scale against the equilibrium concentration of metal in solution to obtain the Freundlich isotherms. An example of Cd retention by the soils in 0.005M $\text{Ca}(\text{NO}_3)_2$, used to simulate a contaminated soil solution, is given in Figure 1. The order of retention was: Tinker > Combustion > Pontchatoula > Cecil > Robins. The scatter in the Robins data was due to lack of retention of Cd by this soil. The retention order corresponds to the order of increasing pH in the soils. The retention of Pb by the soils was similar to Cd retention except for the change in slope for the Tinker soil (Figure 2). The steep slope of the isotherm for the Tinker soil was due to approximately all of the added Pb being retained by the Tinker soil.

Garcia-Miragaya and Page (1976) postulated that the coefficient, K , is a good index of the relative Cd retention affinities of various soils. Overall, $\log K$, and thus Cd retention affinity, decreased in the order: Tinker > Combustion \geq Pontchatoula > Cecil > Robins. However, this order varied slightly between solutions (Table 4). Lead retention affinity decreased in the order: Tinker > Combustion > Pontchatoula > Cecil > Robins, which was similar to Cd. Again, the waste solution composition influenced the retention affinities of the soils for Pb (Table 5).

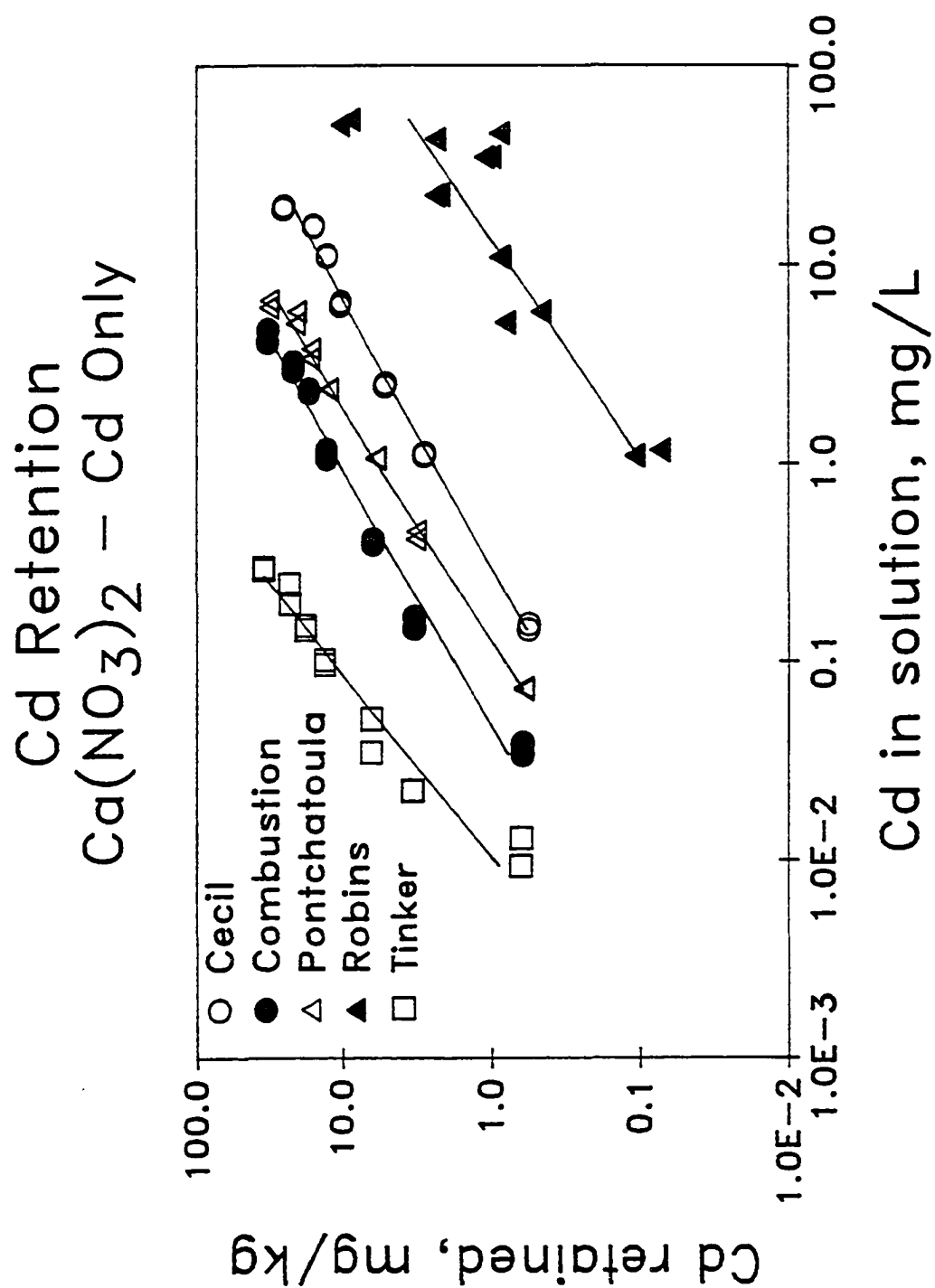


Figure 1. Effect of soil type on Cd retention for the $\text{Ca}(\text{NO}_3)_2$ + Cd only solution.

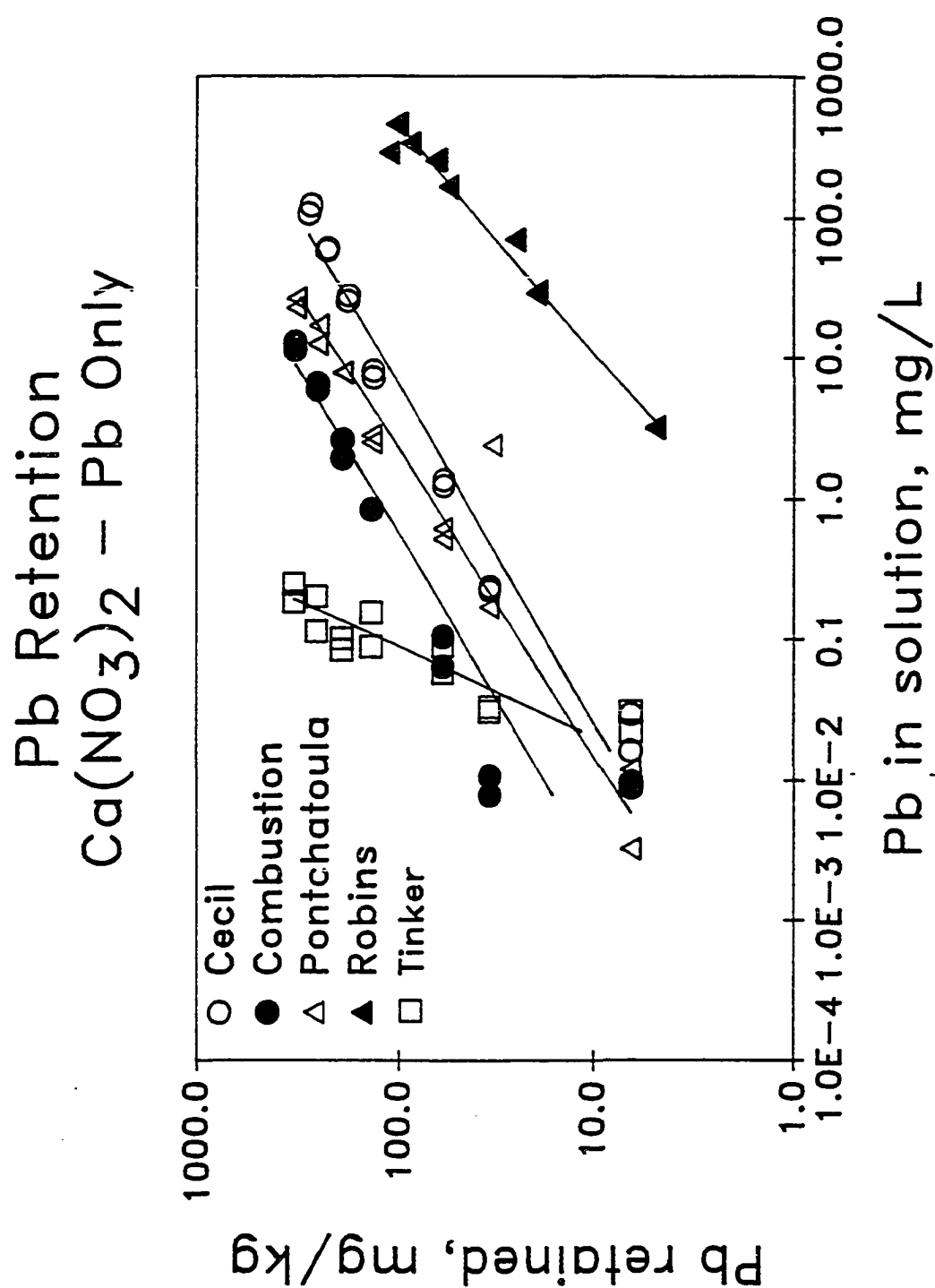


Figure 2. Effect of soil type on Pb retention for the $\text{Ca}(\text{NO}_3)_2$ + Pb only solution.

Table 4. Freundlich parameters for Cd retention by soils within each solution group.

Solution	Soil	Log K	n
Ca(NO ₃) ₂ + Cd	Cecil	0.3930 d [†]	0.7375 c
	Combustion	1.0260 b	0.7720 bc
	Pontchatoula	0.7675 c	0.8475 bc
	Robins	-1.0140 e	0.9055 b
	Tinker	2.1765 a	1.0960 a
Ca(NO ₃) ₂ + Cd+Pb	Cecil	0.2025 d	0.5210 c
	Combustion	0.7110 b	0.5610 c
	Pontchatoula	0.6070 c	0.6955 b
	Robins	-0.7955 e	0.8600 a
	Tinker	1.5710 a	0.6670 b
Syn Leachate	Cecil	-0.5020 b	0.7790 b
	Combustion	-0.5045 b	0.8505 ab
	Pontchatoula	-0.5205 b	0.9040 a
	Robins	-1.1435 c	0.8940 ab
	Tinker	-0.2520 a	0.7840 ab

Table 4. (Continued).

Solution	Soil	Log K	n
Acidic Metals	Cecil	-1.1175 c	0.6790 b
	Combustion	-0.9415 c	0.9655 a
	Pontchatoula	-0.6725 b	0.9385 a
	Robins	-1.0270 c	0.6960 b
	Tinker	0.7370 a	0.6295 b
Oil Field Waste	Cecil	0.2750 c	0.4580 bc
	Combustion	1.1275 b	0.3385 c
	Pontchatoula	1.0495 b	0.4300 bc
	Robins	-1.0280 d	0.6965 a
	Tinker	1.6980 a	0.5760 ab

[†] Log K and n values followed by the same letter within solution groups are not significant at the 0.05 level by the Duncan's multiple range test.

Table 5. Freundlich parameters for Pb retention by soils within each solution group.

Solution	Soil	Log K	n
Ca(NO ₃) ₂ + Pb	Cecil	1.6640 c [†]	0.4170 bc
	Combustion	2.1600 b	0.3180 c
	Pontchatoula	1.8885 bc	0.4450 bc
	Robins	0.3765 d	0.6040 b
	Tinker	3.7700 a	1.6565 a
Ca(NO ₃) ₂ + Pb+Cd	Cecil	1.1485 cd	0.4240 c
	Combustion	2.1350 b	0.3325 c
	Pontchatoula	1.8925 bc	0.4205 c
	Robins	0.3600 d	0.6195 b
	Tinker	3.3290 a	1.1485 a
Syn Leachate	Cecil	0.6590 c	0.6175 d
	Combustion	0.7740 b	0.7355 c
	Pontchatoula	0.3250 d	0.9325 a
	Robins	-0.1955 e	0.7690 b
	Tinker	0.8440 a	0.6150 d

Table 5 (Continued).

Solution	Soil	Log K	n
Acidic Metals	Cecil	0.1130 c	0.6910 b
	Combustion	0.7445 b	0.6925 b
	Pontchatoula	0.2500 c	0.7955 b
	Robins	-0.7330 d	0.6620 b
	Tinker	2.7850 a	1.6495 a
Oil Field Waste	Cecil	1.7035 b	0.3310 a
	Combustion	2.3110 b	0.1920 a
	Pontchatoula	2.1180 b	0.3465 a
	Robins	0.3405 c	0.5505 a
	Tinker	3.1200 a	0.5600 a

† Log K and n values followed by the same letter within solution groups are not significant at the 0.05 level by the Duncan's multiple range test.

Although the Log K values were the same for the two $\text{Ca}(\text{NO}_3)_2$ solutions for both Cd and Pb, the slopes differed (Table 4 and 5) indicating that the presence of the second metal affected the retention of each Cd and Pb, with the presence of Cd having a large effect on Pb retention.

The Freundlich parameters, Log K and n, were correlated with measured soil properties to determine which properties were most important in metal retention. For both Cd and Pb, Log K was correlated to pH, CEC, and sand and silt content (Table 6 and 7). The correlation between metal retention and percent sand was negative, indicating that as the sand content of the soil increased, Cd and Pb retention decreased. The importance of pH in metal retention has been reported before (Santillan-Medrano and Jurinak, 1975; Gadde and Laitinen, 1973, 1974; Cavallaro and McBride, 1980; Elliott, 1983; Kuo and Baker, 1980; LaBauve et al., 1988), as has the importance of CEC (Miller et al., 1976; LaBauve et al., 1988). LaBauve et al. (1988) reported that pH was the soil property that most controlled Cd retention in the system studied, but that percent sand was also important. For Pb, CEC was the measured soil property that most controlled retention, with pH and percent sand also important (LaBauve et al., 1988).

Effect of Solution Composition on Metal Retention

Four synthetic waste solutions and a control solution were used to determine the effect of solution composition on Cd and Pb retention. An example of Cd retention for the five solutions by the Pontchatoula soil is presented in Figure 3. Retention of Pb in the five solutions by the Pontchatoula soil is illustrated in Figure 4. Retention of Cd and Pb was

Table 6. Simple correlation coefficients for Cd relating the Freundlich parameters, Log K and n, to soil properties.

Soil Properties	Log K	n
pH	0.698 **	ns
CEC	0.670 **	ns
Sand, %	-0.679 **	ns
Silt, %	0.530 **	ns

*, ** significant at 0.05 and 0.01 levels, respectively.

ns = not significant.

Table 7. Simple correlation coefficients for Pb relating the Freundlich parameters, Log K and n, to soil properties.

Soil Properties	Log K	n
pH	0.696 **	ns
CEC	0.666 **	0.448 *
Sand, %	-0.697 **	ns
Silt, %	0.532 **	ns

*, ** significant at 0.05 and 0.01 levels, respectively.

ns = not significant.

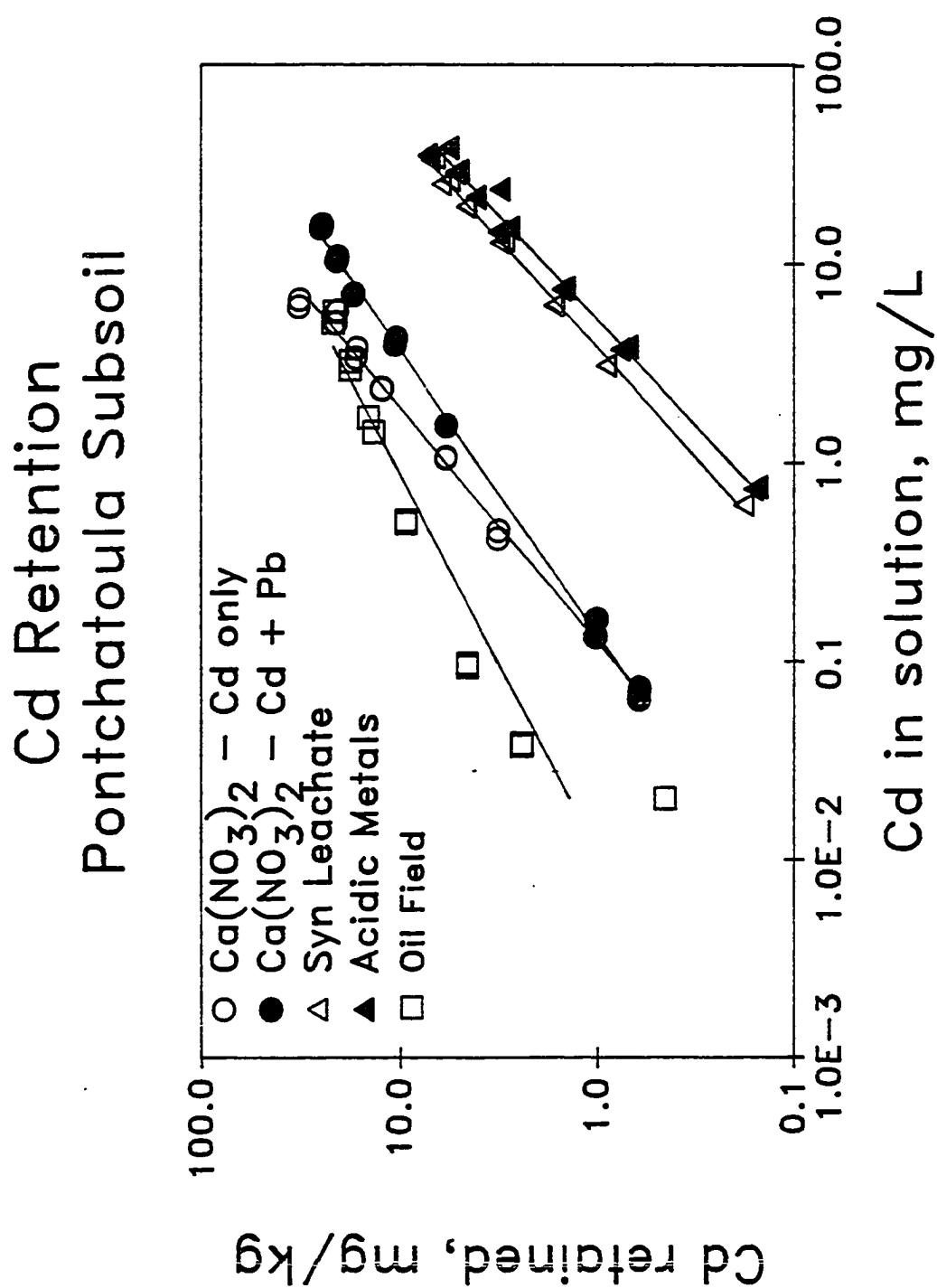


Figure 3. Effect of solution composition on Cd retention by Pontchatoula subsoil.

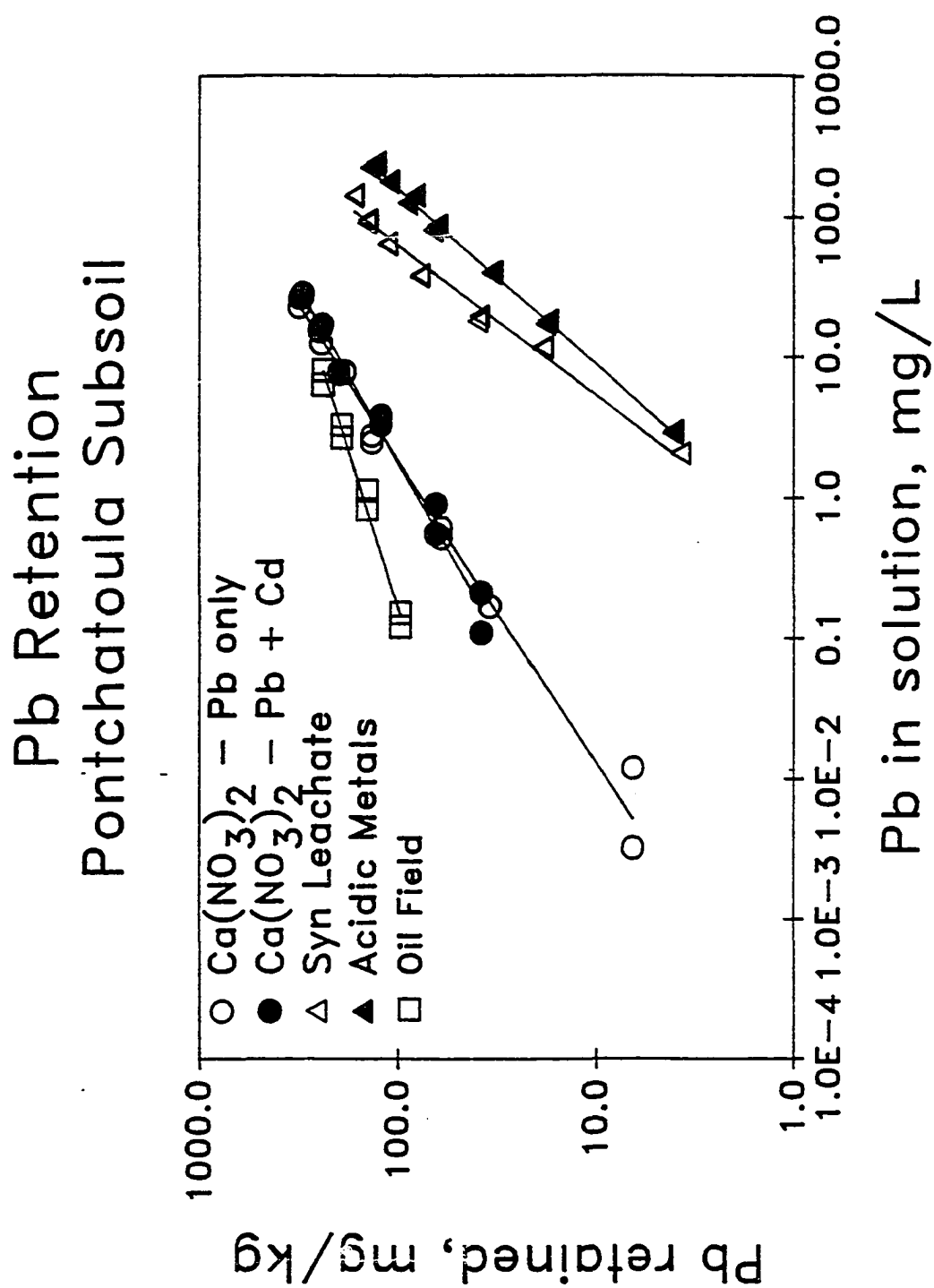


Figure 4. Effect of solution composition on Pb retention by Pontchatoula subsoil.

least in the acidic metals waste and synthetic leachate and greatest in the oil field waste. Comparing the two $\text{Ca}(\text{NO}_3)_2$ solutions for Cd retention (Figure 3), it is evident that there is competition for retention sites at higher concentrations of Cd and Pb - the two isotherms diverge at higher concentrations, with greater retention in the Cd only solution. This competition is not evident in Pb retention (Figure 4) as Pb is retained more strongly than Cd. Retention was enhanced in the oil field waste compared to the dilute salt solution. It is probable that the Cr(III) in the oil field waste precipitated as the hydroxide, with the metals co-precipitating with the Cr(III). As pH increased above pH 4, Griffin and Shimp (1978) reported that precipitation of Cr(III) as an amorphous hydrated hydroxide occurred. Cadmium and Pb retention was reduced in the synthetic landfill leachate, probably due to complexation of the metals by the organics in the solution. Knox and Jones (1979) reported that three sanitary landfill leachates tested were able to complex Cd to some extent, although their ability to do so varied. A synthetic anaerobic landfill leachate reduced Cd retention by soils in a study by LaBauve et al. (1988). Reduced retention of Cd due to complexation has also been reported by Doner (1978), Benjamin and Leckie (1982), and Garcia-Miragaya and Page (1976). Brown (1979) reported that complexation reduced Pb retention. Retention of Cd and Pb was also reduced for the acidic metals waste due to the low pH (pH 2) of the waste and competition with other metals in the waste for soil retention sites. Huang et al. (1977) reported that for hydrous oxides and whole soils, retention followed the order: $\text{Cu(II)} > \text{Zn(II)} > \text{Pb(II)} > \text{Cd(II)}$. Therefore, Cu and Zn would have been preferentially retained by the soils, reducing Cd and Pb retention.

Overall, the Freundlich parameter, Log K, and thus retention affinity of Cd, decreased in the order: $\text{Ca}(\text{NO}_3)_2 + \text{Cd only} \geq \text{oil field} > \text{Ca}(\text{NO}_3)_2 + \text{Cd+Pb} > \text{synthetic leachate} \geq \text{acidic metals}$. Again, the order was dependent on soils (Table 8). For Pb, Log K overall decreased in the order: $\text{Ca}(\text{NO}_3)_2 + \text{Pb only} \geq \text{oil field} \geq \text{Ca}(\text{NO}_3)_2 + \text{Pb+Cd} > \text{acidic metals} \geq \text{synthetic leachate}$ (Table 9). It should be noted that retention of Cd and Pb in the acidic metals waste was greater than in the synthetic leachate for the Tinker soil because the high pH, buffering capacity, and CEC of the Tinker soil was able to neutralize the acid in the waste and because the high retention capacity of the soil greatly reduced competition for retention sites.

SUMMARY AND CONCLUSIONS

The retention of Cd by the five subsoil materials followed the order: Tinker > Combustion \geq Pontchatoula > Cecil > Robins. For Pb, the order was: Tinker > Combustion > Pontchatoula > Cecil > Robins. The Freundlich parameter, Log K, for both Cd and Pb was correlated with pH, CEC, and percent silt and negatively correlated with percent sand. Of the parameters measured, therefore, pH, CEC, and silt and sand content of the soil were the properties most important in Cd and Pb retention. As pH, CEC, and percent silt increased in the soil, retention increased, while as percent sand increased in the soil, retention decreased.

The composition of the solution containing the metals influenced Cd and Pb retention by soil. For Cd, retention followed the order: $\text{Ca}(\text{NO}_3)_2 + \text{Cd only} \geq \text{oil field waste} > \text{Ca}(\text{NO}_3)_2 + \text{Cd+Pb} > \text{synthetic leachate} \geq \text{acidic metal}$. For Pb, the order was: $\text{Ca}(\text{NO}_3)_2 + \text{Pb only} \geq \text{oil field} \geq$

Table 8. Freundlich parameters and r values for Cd retention by solutions within each soil group.

Soil	Solution	Log K	n	r
Cecil	Ca(NO ₃) ₂ + Cd	0.3930 a [†]	0.7375 ab	0.996
	Ca(NO ₃) ₂ + Cd+Pb	0.2025 a	0.5210 bc	0.994
	Syn Leachate	-0.5020 b	0.7790 a	0.986
	Acidic Metals	-1.1175 c	0.6790 abc	0.928
	Oil Field	0.2750 a	0.4580 c	0.925
Combustion	Ca(NO ₃) ₂ + Cd	1.0260 b	0.7720 c	0.990
	Ca(NO ₃) ₂ + Cd+Pb	0.7110 c	0.5610 d	0.995
	Syn Leachate	-0.5045 d	0.8505 b	0.975
	Acidic Metals	-0.9415 e	0.9655 a	0.995
	Oil Field	1.1275 a	0.3385 e	0.924
Pontchatoula	Ca(NO ₃) ₂ + Cd	0.7675 b	0.8475 b	0.997
	Ca(NO ₃) ₂ + Cd+Pb	0.6070 c	0.6955 c	0.999
	Syn Leachate	-0.5205 d	0.9040 ab	0.998
	Acidic Metals	-0.6725 e	0.9385 a	0.995
	Oil Field	1.0495 a	0.4300 d	0.940

Table 8. (Continued).

Soil	Solution	Log K	n	r
Robins	Ca(NO ₃) ₂ + Cd	-1.0140 b	0.9055 a	0.873
	Ca(NO ₃) ₂ + Cd+Pb	-0.7955 a	0.8600 ab	0.952
	Syn Leachate	-1.1435 c	0.8940 a	0.989
	Acidic Metals	-1.0270 b	0.6960 b	0.989
	Oil Field	-1.0280 b	0.6965 b	0.980
Tinker	Ca(NO ₃) ₂ + Cd	2.1765 a	1.0960 a	0.972
	Ca(NO ₃) ₂ + Cd+Pb	1.5710 b	0.6670 b	0.951
	Syn Leachate	-0.2520 d	0.7840 b	0.997
	Acidic Metals	0.7370 c	0.6295 b	0.984
	Oil Field	1.6980 b	0.5760 b	0.968

† Log K and n values followed by the same letter within soil groups are not significant at the 0.05 level by the Duncan's multiple range test.

Table 9. Freundlich parameters and r values for Pb retention by solutions within each soil group.

Soil	Solution	Log K	n	r
Cecil	$\text{Ca}(\text{NO}_3)_2 + \text{Pb}$	1.6640 a [†]	0.4170 c	0.983
	$\text{Ca}(\text{NO}_3)_2 + \text{Pb}+\text{Cd}$	1.1485 ab	0.4240 c	0.981
	Syn Leachate	0.6590 bc	0.6175 b	1.000
	Acidic Metals	0.1130 c	0.6910 a	0.995
	Oil Field	1.7035 a	0.3310 d	0.939
Combustion	$\text{Ca}(\text{NO}_3)_2 + \text{Pb}$	2.1600 b	0.3180 c	0.928
	$\text{Ca}(\text{NO}_3)_2 + \text{Pb}+\text{Cd}$	2.1350 c	0.3325 c	0.974
	Syn Leachate	0.7740 d	0.7355 a	0.998
	Acidic Metals	0.7845 e	0.6925 b	0.960
	Oil Field	2.3110 a	0.1920 b	0.981
Pontchatoula	$\text{Ca}(\text{NO}_3)_2 + \text{Pb}$	1.8885 b	0.4450 b	0.962
	$\text{Ca}(\text{NO}_3)_2 + \text{Pb}+\text{Cd}$	1.8925 b	0.4205 b	0.992
	Syn Leachate	0.3250 c	0.9325 a	0.993
	Acidic Metals	0.2500 c	0.3465 b	0.999
	Oil Field	2.1180 a	0.3465 b	0.994

Table 9. (Continued).

Soil	Solution	Log K	n	r
Robins	$\text{Ca}(\text{NO}_3)_2 + \text{Pb}$	0.3765 a	0.6040 b	0.989
	$\text{Ca}(\text{NO}_3)_2 + \text{Pb}+\text{Cd}$	0.3600 a	0.6195 ab	0.957
	Syn Leachate	-0.1955 b	0.7690 a	0.998
	Acidic Metals	-0.7330 c	0.6620 ab	0.898
	Oil Field	0.3405 a	0.5505 b	0.995
Tinker	$\text{Ca}(\text{NO}_3)_2 + \text{Pb}$	3.7700 a	1.6565 a	0.908
	$\text{Ca}(\text{NO}_3)_2 + \text{Pb}+\text{Cd}$	3.3290 ab	1.1485 ab	0.936
	Syn Leachate	0.8440 c	0.6150 b	0.996
	Acidic Metals	2.7850 b	1.6495 a	0.784
	Oil Field	3.1200 ab	0.5600 b	0.814

† Log K and n values followed by the same letter within soil groups are not significant at the 0.05 level by the Duncan's multiple range test.

$\text{Ca}(\text{NO}_3)_2 + \text{Pb} + \text{Cd} > \text{acidic metals} \geq \text{synthetic leachate}$. Retention of Cd and Pb in the oil field waste was likely enhanced by co-precipitation of the metals with Cr(III) to an amorphous hydroxide. Retention was reduced in the synthetic leachate due to complexation with organics and in the acidic metals waste due to the low pH of the waste and competition with other metals.

The importance of soil/solution interactions should be noted. For example, the Tinker soil showed reduced retention for the synthetic leachate versus the acidic metals waste, because of its higher pH and buffering capacity, while other soils, because of their lower pH and/or poor buffering, showed the opposite trend, enhanced retention for the synthetic leachate versus the acidic metals waste.

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CHAPTER 6

THE EFFECT OF SOIL TYPE, SOLUTE CONCENTRATION, SOLUTION
COMPOSITION, AND OXYGEN STATUS ON CADMIUM AND LEAD
RETENTION AND CHEMICAL FRACTIONATION

ABSTRACT

Determination of the factors affecting metal retention and mobility in soils is of interest because of the risk of groundwater contamination, especially under hazardous waste disposal sites. This laboratory study was conducted to determine the effect of a soil's physical and chemical properties, solute concentration, waste solution composition, and redox status on the retention and release of Cd and Pb. Five soils of varying properties were chosen. Four waste solutions were used with the metals: 0.005M $\text{Ca}(\text{NO}_3)_2$, a synthetic municipal landfill leachate, a synthetic acidic metals waste, and a synthetic oil field waste. The suspensions were purged with air or Ar for 7 days to maintain aerobic or anoxic conditions, then the purging gases were switched for a second 7-day period.

For all the soils and all the solutions, Pb was retained to a greater degree than was Cd. Retention of both metals followed the soils order: Tinker > Cecil \geq Pontchatoula \geq Combustion > Robins; that is greatest retention in the soil with the highest pH, clay content, CEC, and

Fe oxide content. At the lower concentrations of Pb and Cd, greater proportions of the metals were retained by the soil. Metal removal by soil from the four solutions decreased in the order: $\text{Ca}(\text{NO}_3)_2$ > oil field > acidic metals \geq synthetic leachate. Typically, those soil-suspensions purged with air immobilized more metal than those purged with Ar.

The sequential fractionation studies indicated that Cd was retained in more available forms than was Pb. Lead availability between soils followed the same trends as Pb retention - most available in the Robins soil and least available in the Tinker soil. Solution composition did affect availability of retained Pb.

INTRODUCTION

The transport of metals to groundwater below hazardous waste sites is of great environmental concern. The movement of a particular metal is determined by the amount and form of the metal, the soil's chemical and physical properties, and the composition of the soil or waste solution with which the metal is associated. The soil properties affecting metal retention/release and transport include bulk density, surface area, particle-size distribution, pH, redox status, ion exchange capacity, amount of organic matter, type and amount of metal oxides, and type and amount of clay minerals (Amacher et al., 1986). Soils with a wide range of these properties were selected for this study except that all of the subsoils materials had typically low levels of organic matter. Soil organic matter, at levels commonly found in surface soils and sediments, is one of the primary immobilizing processes for trace and toxic metals (Gerritse and van Driel, 1984; Levi-Minzi et al, 1976). Subsoils, usually

beginning 15 cm to 30 cm beneath the surface, generally contain so little naturally-occurring organic matter that it becomes important to focus on other metal retention processes in the region between surface soils and groundwater.

There are a number of reviews and reports on factors affecting the mobility and plant availability of trace and toxic metals. Much of this work has focused on topsoils or sediments containing an appreciable amount of naturally occurring organic matter compared to subsoils. Soil humic material is known to be very effective in immobilizing most trace and toxic metals. Since subsoils contain much less organic matter and are the primary transport media if metals contamination of groundwater is to occur, research efforts should be directed toward processes regulating metal mobility in subsoils.

Solution composition will also greatly affect metal retention and movement. The greater the concentration of a specific pollutant in the leachate, the more likely it is to move through the soil. Complexation of Cd (Benjamin and Leckie, 1982; Garcia-Miragaya and Page, 1976; Knox and Jones, 1979; LaBauve et al., 1988) and Pb (Brown, 1979; LaBauve et al., 1988) have been reported to decrease Cd and Pb retention by soils.

The objectives of this study were to determine the effect of soil type, solute concentration, solution composition, and redox status on Pb and Cd retention/release and chemical fractionation.

MATERIALS AND METHODS

Soil Selection and Characterization

Five subsoil materials of different physical and chemical properties were selected for this study to determine the effect of the soil's physical and chemical properties on Cd and Pb retention. The designation and classification of the soil materials are presented in Table 1, and selected soil properties are listed in Table 2. The pH of the samples was determined in a 1:1 soil:water paste (McLean, 1982). Cation exchange capacity (CEC) was determined by summing the major cations (Ca, Mg, Na, K, and Al) extracted with 0.1M BaCl₂ (adapted from Rhoades, 1982). Particle-size distribution was determined by the hydrometer method (Gee and Bauder, 1986). The Mn oxide content of the samples was extracted using pH 2, 0.1M hydroxylamine hydrochloride (NH₂OH•HCl) (Chao, 1972). Amorphous Fe oxides were determined using 0.25M hydroxylamine hydrochloride-0.25M HCl (Chao and Zhou, 1983). Free Fe oxides were determined using the dithionite-citrate-bicarbonate (DCB) method (Mehra and Jackson, 1960).

Retention of Cd and Pb

The subsoil material was air-dried and ground to pass a 2-mm sieve prior to use. The solutions used in this study are listed in Table 3. The metals studied were Cd and Pb. The effect of metal concentration on retention was examined using a high-metal concentration solution (500 mg•L⁻¹ Pb and 50 mg•L⁻¹ Cd) and a low-metal concentration solution (50 mg•L⁻¹ Pb and 5 mg•L⁻¹ Cd). The co-waste solutions were chosen to simulate a soil solution and various waste materials. The experiments were

Table 1. Classification of soil materials used in batch study.

Designation	Soil Series	Taxonomic Classification
Cecil	Cecil	clayey, kaolinitic, thermic, Typic Hapludult
Combustion	unknown	
Pontchatoula	unknown	
Robins AFB	Norfolk	fine-loamy, siliceous, thermic, Typic Paleudult
Tinker	Vernon	fine, mixed, thermic, Typic Ustochrepts

Table 2. Selected chemical and physical properties of soils used in batch study.

Soil	pH	CEC	MnO ₂	Amorph.	Total	Sand	Silt	Clay
				Fe ₂ O ₃	Fe ₂ O ₃			
		cmol (+)/kg			%			
Cecil	4.92	2.58	0.005	0.051	1.030	18	9	73
Combustion	7.00	10.37	0.071	0.141	0.213	17	54	29
Pontchatoula	6.49	15.33	0.005	0.034	0.092	27	36	37
Robins AFB	3.50	1.31	0.001	0.014	0.059	72	13	15
Tinker AFB	7.60	28.94	0.015	0.034	0.291	0	45	55

Table 3. Composition of synthetic waste solutions used in batch study.

Waste Solution	Composition
$\text{Ca}(\text{NO}_3)_2^\dagger$	0.005M $\text{Ca}(\text{NO}_3)_2$
Synthetic Municipal Landfill	0.15M sodium acetate
Leachate (Aerobic)‡	0.15M acetic acid
	0.050M glycine
	0.007M salicylic acid
Acidic Metals Waste	100 mg•L ⁻¹ Cu 200 mg•L ⁻¹ Ni
	200 mg•L ⁻¹ Cr 300 mg•L ⁻¹ Zn
	HCl to pH 2
Oil Field Waste§	50 mg•L ⁻¹ Ba 10 mg•L ⁻¹ Cr(III)
	25 mg•L ⁻¹ naphthalene
Each solution also contained either:	
(a) 500 mg•L ⁻¹ Pb + 50 mg•L ⁻¹ Cd, or	
(b) 50 mg•L ⁻¹ Pb + 5 mg•L ⁻¹ Cd	

[†]Amacher et al., 1986.

[‡]Stanforth et al., 1979.

[§]Pardue (unpubl.).

performed in duplicate. A flow diagram of the procedure is presented in Figure 1. Twenty (20) g. of each soil material was added to four 250-mL centrifuge bottles. To two of the soils, 200 mL of the high-metal concentration solution was added. To each of the other two bottles, 200-mL of the low-metal concentration solution was added. To determine the effect of redox status on metal retention, the soil-suspensions were purged twice daily; one sample of each of the two solutions was purged with air containing 0.03% CO_2 (designated O_2), and the other was purged with Ar containing 0.03% CO_2 . The soil-solutions were shaken continuously on a reciprocating box shaker at $140 \text{ osc} \cdot \text{min}^{-1}$. Samples were taken at 24-hr intervals, 6 days a week, filtered, acidified, and analyzed by ICP. After 7 days, the purgings were reversed such that those soil-solutions purged with air were then purged with Ar and vice-versa to simulate a change in the soil oxidation status, such as a rising and falling water table.

The redox potential readings were typically measured on Days 1, 4, 7, 11, and 14 using a platinum (Pt) electrode and an Ag/AgCl reference electrode, as illustrated in Figure 2. The pH of the soil solutions was determined at the end of each purge cycle.

Sequential Fractionation of Retained Cd and Pb

The soil samples at Day 7 and 14 were extracted to determine selected chemical forms of Cd and Pb in the soil using the sequential fractionation scheme outlined in Figure 3. The scheme consists of running the procedures for extracting Mn oxides, amorphous Fe oxides, and free Fe oxides in sequence preceded by extractions with a neutral salt (BaCl_2) and a chelating agent (EDTA) to determine weakly and strongly sorbed Cd and

Batch Kinetic Study

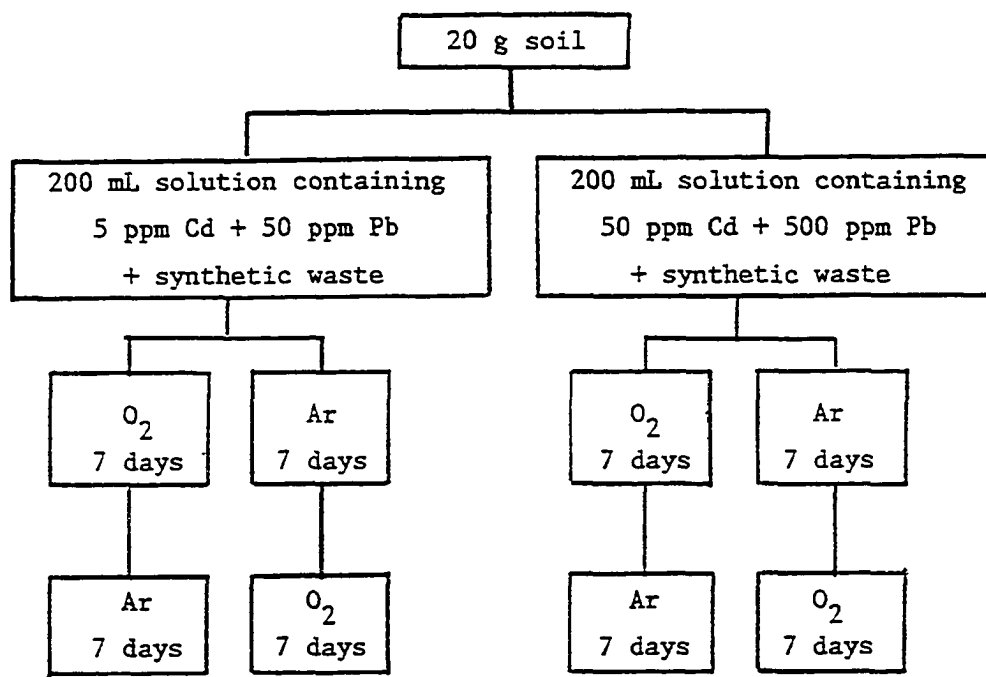


Figure 1. Design of batch kinetic study.

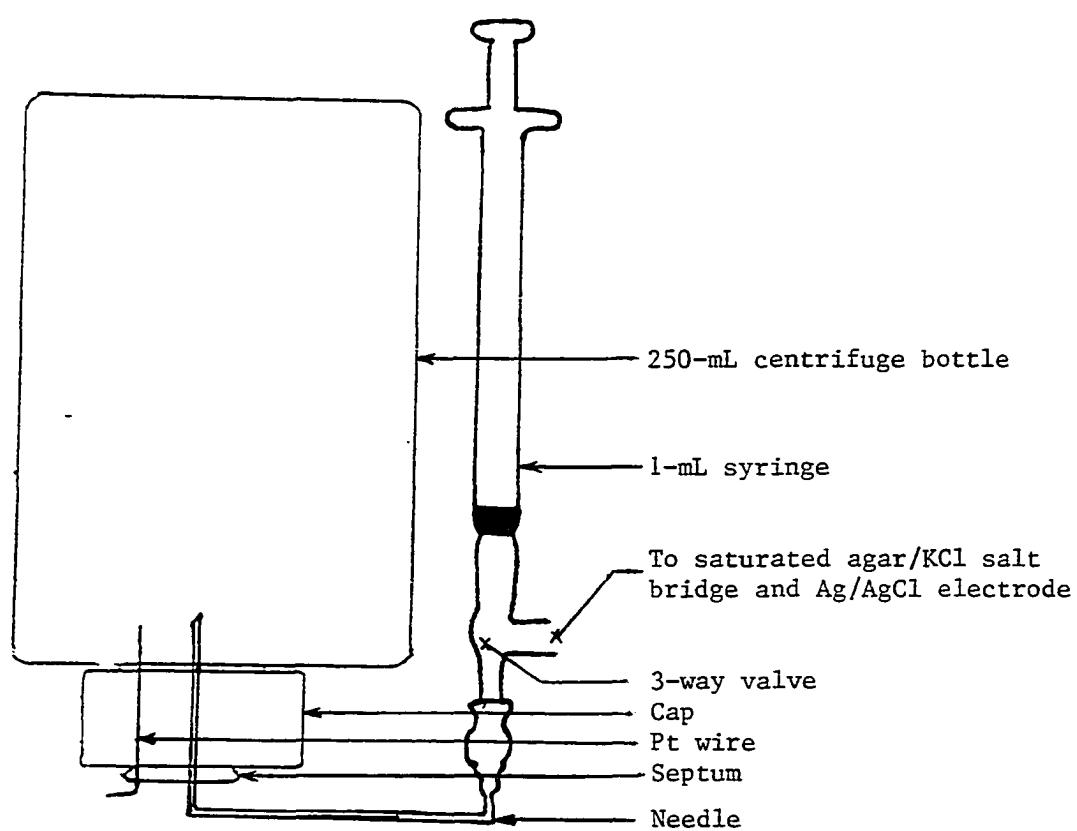


Figure 2. Batch kinetic reactor for determining redox potential.

SEQUENTIAL FRACTIONATION SCHEME

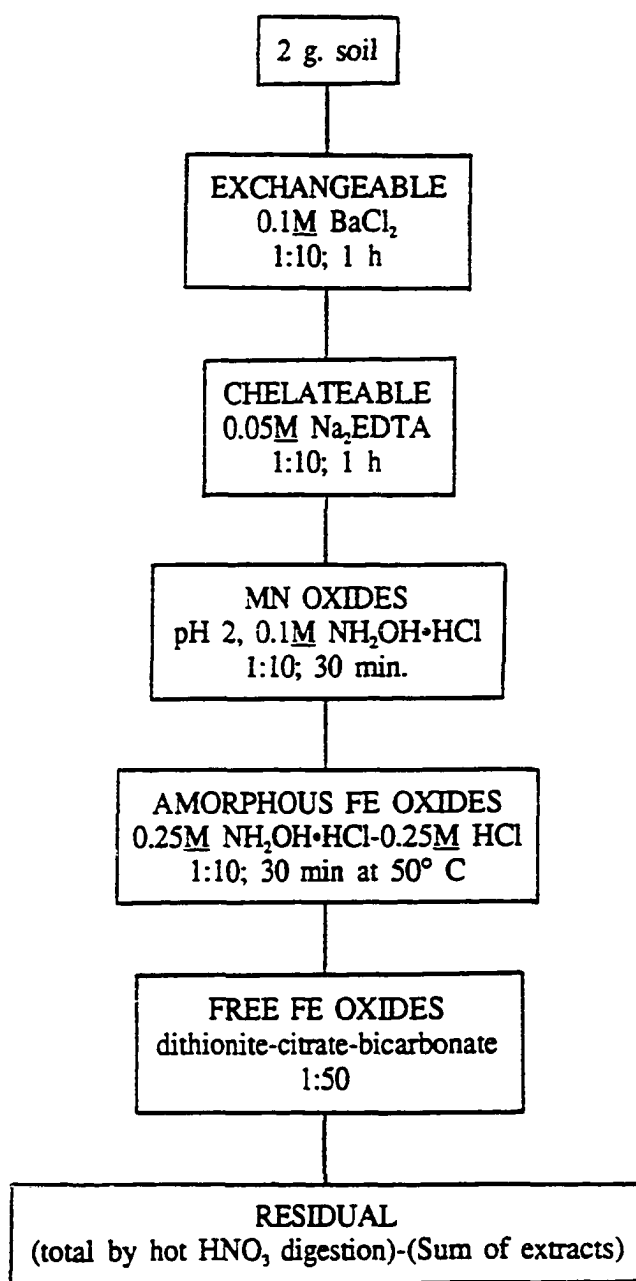


Figure 3. Sequential fractionation scheme used to determine the distribution of retained Cd and Pb.

Pb. This scheme is not based on any particular scheme in the literature, but is similar to several used by other investigators (Pickering, 1981; Salomons and Forstner, 1984). The extractants in the sequential fractionation scheme were used to extract Cd and Pb associated with the following chemical phases in soils: (1) 0.1M BaCl_2 - weakly sorbed and exchangeable Cd and Pb; (2) 0.05M EDTA - chelateable and strongly sorbed Cd and Pb; (3) pH 2, 0.1M $\text{NH}_2\text{OH}\cdot\text{HCl}$ - Cd and Pb associated with Mn oxides; (4) 0.25M $\text{NH}_2\text{OH}\cdot\text{HCl}$ -0.25M HCl - Cd and Pb associated with amorphous Fe oxides; and (5) DCB - Cd and Pb associated with free Fe oxides. The BaCl_2 and EDTA extractants do not dissolve a particular mineral phase, thus Cd and Pb sorbed to a variety of mineral phases including some metal oxides may be extracted with these extractants. The metal oxide extractants extract strongly sorbed Cd and Pb not extracted by the BaCl_2 and EDTA as well as Cd and Pb coprecipitated with the metal oxides.

RESULTS AND DISCUSSION

Retention of Cd and Pb

Uncontaminated soils were amended with two concentrations of Pb and Cd ($5 \text{ mg}\cdot\text{L}^{-1}$ Cd plus $50 \text{ mg}\cdot\text{L}^{-1}$ Pb and $50 \text{ mg}\cdot\text{L}^{-1}$ Cd plus $500 \text{ mg}\cdot\text{L}^{-1}$ Pb) in four synthetic soil or waste solutions ($\text{Ca}(\text{NO}_3)_2$, synthetic municipal landfill leachate, synthetic acidic metals waste, and oil field waste) and equilibrated under air (O_2) or Ar atmospheres. The concentration of Pb and Cd in the soil solution was determined six times per week. The daily concentrations were compared to the concentration at the start of the experiment to obtain values of C/C_0 . These concentration ratios were plotted against time. However, no clear trends with time were observed.

For all the soils and all the solutions, Pb was retained more strongly by the soil than was Cd. Retention of both metals for all solution types was in the order: Tinker > Cecil \geq Pontchatoula \geq Combustion > Robins (Table 4). The Tinker control soil retained most of the metal added to it, while the Robins material retained very little of the metal added (Figure 4 vs. Figure 5). The Tinker soil had a high pH, high CEC, and high clay content, and, compared to the Robins and Pontchatoula soils, higher Fe oxides. The Robins soil, on the other hand, was a sandy material with a low pH, low CEC, and low oxides content. Korte et al. (1976) and Fuller (1978) found that the movement of Pb was related to soil texture, with Pb migrating deeper in the column for those soils coarsest in texture. LaBauve et al. (1988) reported that Cd and Pb were retained more by soils with higher clay contents.

At the lower concentration of Pb and Cd, greater proportions of the metals were retained by the soil, leading to lower C/Co values. This effect is due to higher concentrations approaching or exceeding the immobilization capacity of the different retention processes in the soil (Fuller, 1980). This trend was more apparent in the $\text{Ca}(\text{NO}_3)_2$ solutions than in the synthetic leachate and acidic metals solutions, the latter two tending to keep metals in solution. The effect of concentration on metal retention was more apparent in the Cecil, Combustion, and Pontchatoula soils than in the Robins and Tinker soils. This is because, even at lower metal concentrations, the capacity of some of the retention processes of the Robins soil was exceeded. The retention capacity of the Tinker soil was so great that even at high metal concentrations, the soil retained most of the added metals.

Table 4. Effect of soil type on metal retention.

Metal	Conc(mg•L ⁻¹)	Soil type	Concentration, C/Co [†]
Cd	5	Cecil	0.785 b [†]
		Combustion	0.708 c
		Pontchatoula	0.729 c
		Robins	0.921 a
		Tinker	0.233 d
	50	Cecil	0.878 b
		Combustion	0.828 c
		Pontchatoula	0.787 d
		Robins	0.919 a
		Tinker	0.365 e

Table 4. (Continued).

Metal	Conc(mg•L ⁻¹)	Soil type	Concentration, C/Co [†]
Pb	50	Cecil	0.319 c
		Combustion	0.210 d
		Pontchatoula	0.385 b
		Robins	0.789 a
		Tinker	0.087 e
	500	Cecil	0.614 b
		Combustion	0.483 d
		Pontchatoula	0.550 c
		Robins	0.863 a
		Tinker	0.138 e

[†] C/Co pooled across waste type, purging time period, and purging gas.

[‡] Concentration values followed by the same letter within metal-level groups are not significantly different at the 0.05 level by the Duncan's Multiple Range Test.

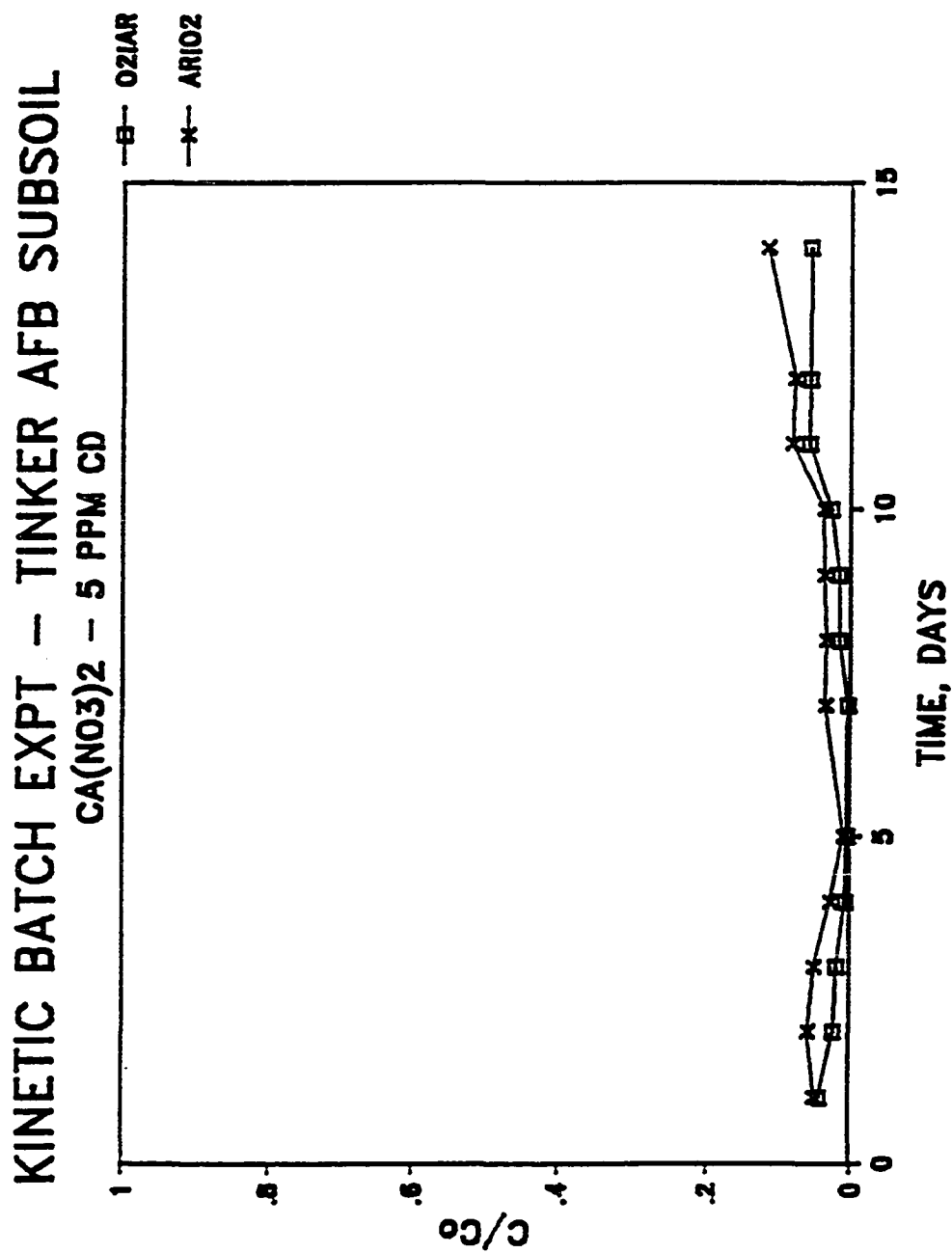


Figure 4. Retention of 5 mg·L⁻¹ Cd in 0.005M Ca(NO₃)₂ by Tinker subsoil.

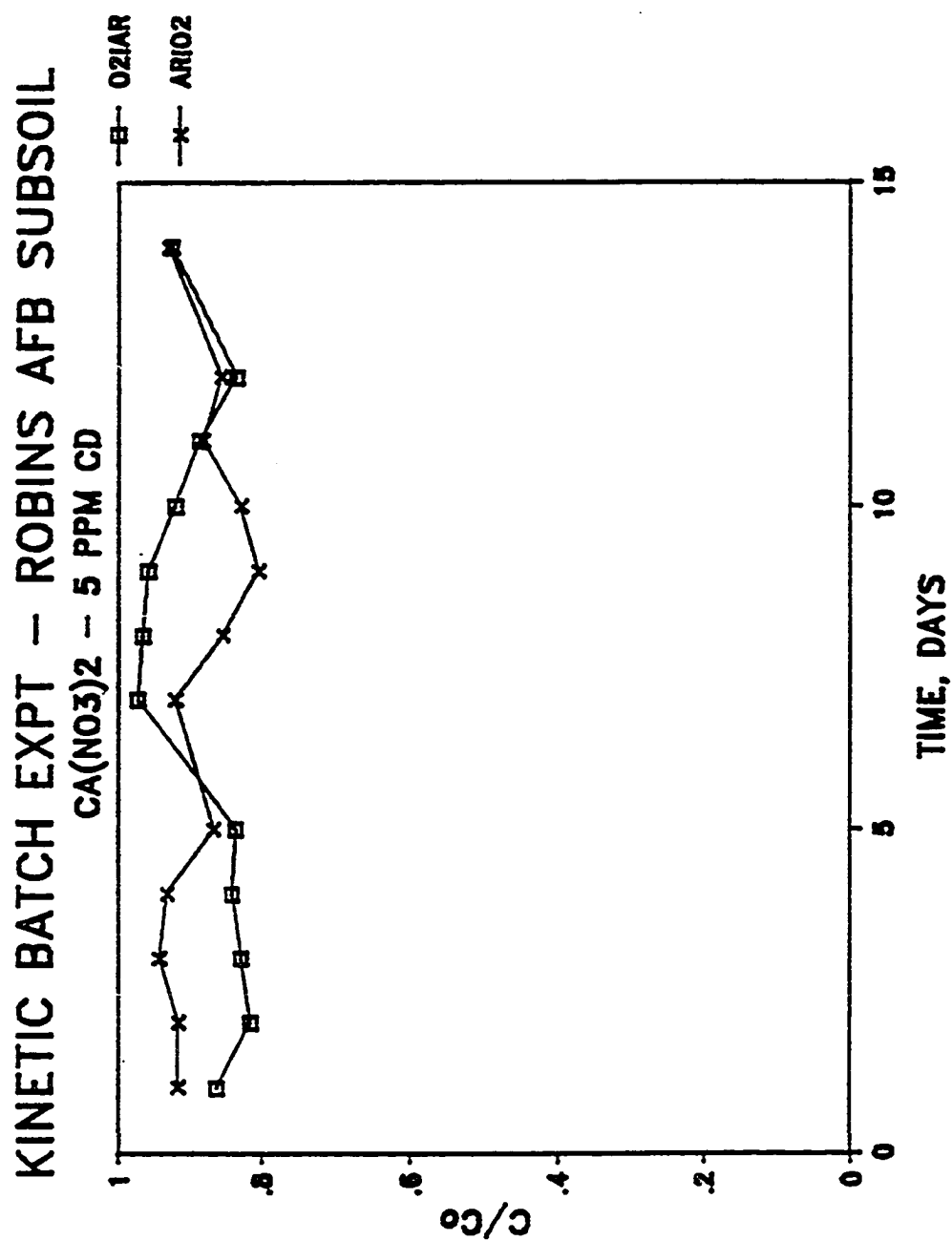


Figure 5. Retention of 5 mg·L⁻¹ Cd in 0.005M Ca(NO₃)₂ by Robins subsoil.

Comparing the effect of a simulated soil solution and three co-waste solutions, the order of metal removal (immobilization) from solution was: $\text{Ca}(\text{NO}_3)_2 > \text{oil field waste} > \text{acidic metals waste} \geq \text{synthetic leachate}$ (Table 5). To illustrate these differences, the four waste materials are compared for the Tinker soil at the $5 \text{ mg} \cdot \text{L}^{-1}$ level in Figures 4 and 6-8. The synthetic leachate solution contained competing cations, organics, and complexing anions which reduced Pb and Cd retention. In the presence of this waste, Pb and Cd retention were greatly reduced even for the Tinker soil (Figure 6 vs. Figures 4, 7, 8), which did not display much reduction in retention in the presence of the acidic metals waste. This indicates the importance of complexing anions and organics in Pb and Cd transport to groundwater. LaBauve et al. (1988) reported that Pb retention by soils was reduced in the presence of a synthetic anaerobic landfill leachate. Brown (1979) also reported that complexation reduced Pb retention. Knox and Jones (1979) reported that three sanitary landfill leachates tested were able to complex Cd to some extent. Reduced Cd retention due to complexation has also been reported by Doner (1978), Benjamin and Leckie (1982), Garcia-Miragaya and Page (1976).

The synthetic leachate solutions were rose-to-wine colored, with the lightest color associated with the Tinker soil and the darkest color with the Robins. soil. The color typically deepened with time. The solution, prior to addition to the soil, was colorless, indicating that the formation of the complex required an interaction with the soil. The easily reducible Mn oxides may have reacted with organic ligands leading to polymerization of the organic ligands and resulting in colorization of the solution (McBride, 1987; Shindo and Huang, 1982, 1984; Stone and Morgan, 1984a,b).

Table 5. Effect of waste type on metal retention.

Metal	Conc(mg•L ⁻¹)	Waste	Concentration, C/Co [†]
Cd	5	Ca(NO ₃) ₂	0.491 d [‡]
		Syn Leach	0.817 a
		Acid	0.752 b
		Oil Field	0.638 c
	50	Ca(NO ₃) ₂	0.640 d
		Syn Leach	0.849 a
		Acid	0.800 b
		Oil Field	0.728 c

Table 5. (Continued).

Metal	Conc(mg•L ⁻¹)	Waste	Concentration, C/Co [†]
Pb	50	Ca(NO ₃) ₂	0.161 c
		Syn Leach	0.527 a
		Acid	0.514 a
		Oil Field	0.208 b
	500	Ca(NO ₃) ₂	0.378 d
		Syn Leach	0.662 a
		Acid	0.601 b
		Oil Field	0.473 c

[†] C/Co pooled across soil type, purging time period, and purging gas.

[‡] Concentration values followed by the same letter within metal-level groups are not significantly different at the 0.05 level by the Duncan's Multiple Range Test.

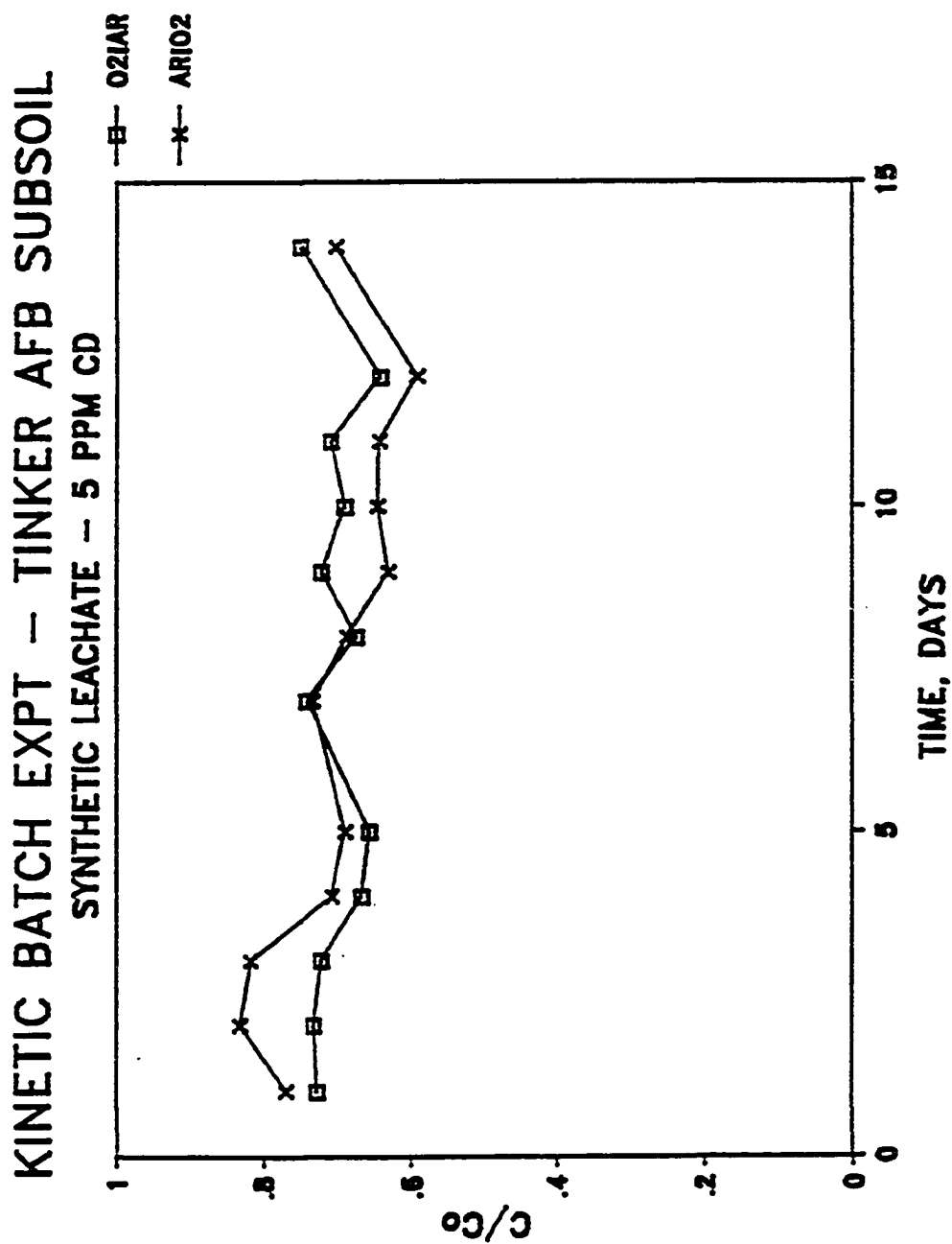


Figure 6. Retention of $5 \text{ mg} \cdot \text{L}^{-1}$ Cd in synthetic leachate by Tinker subsoil.

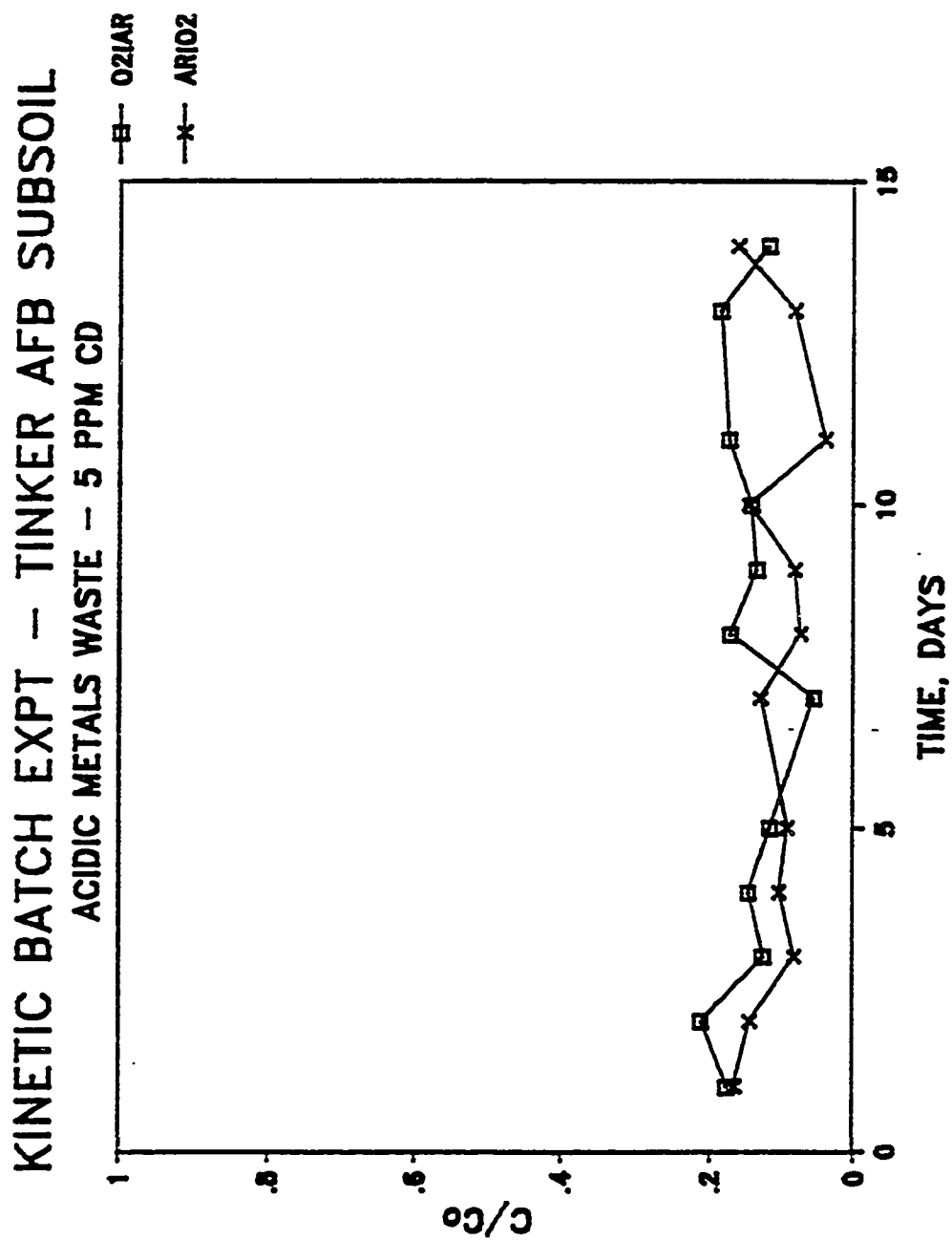


Figure 7. Retention of $5 \text{ mg} \cdot \text{L}^{-1}$ Cd in acidic metals waste by Tinker subsoil.

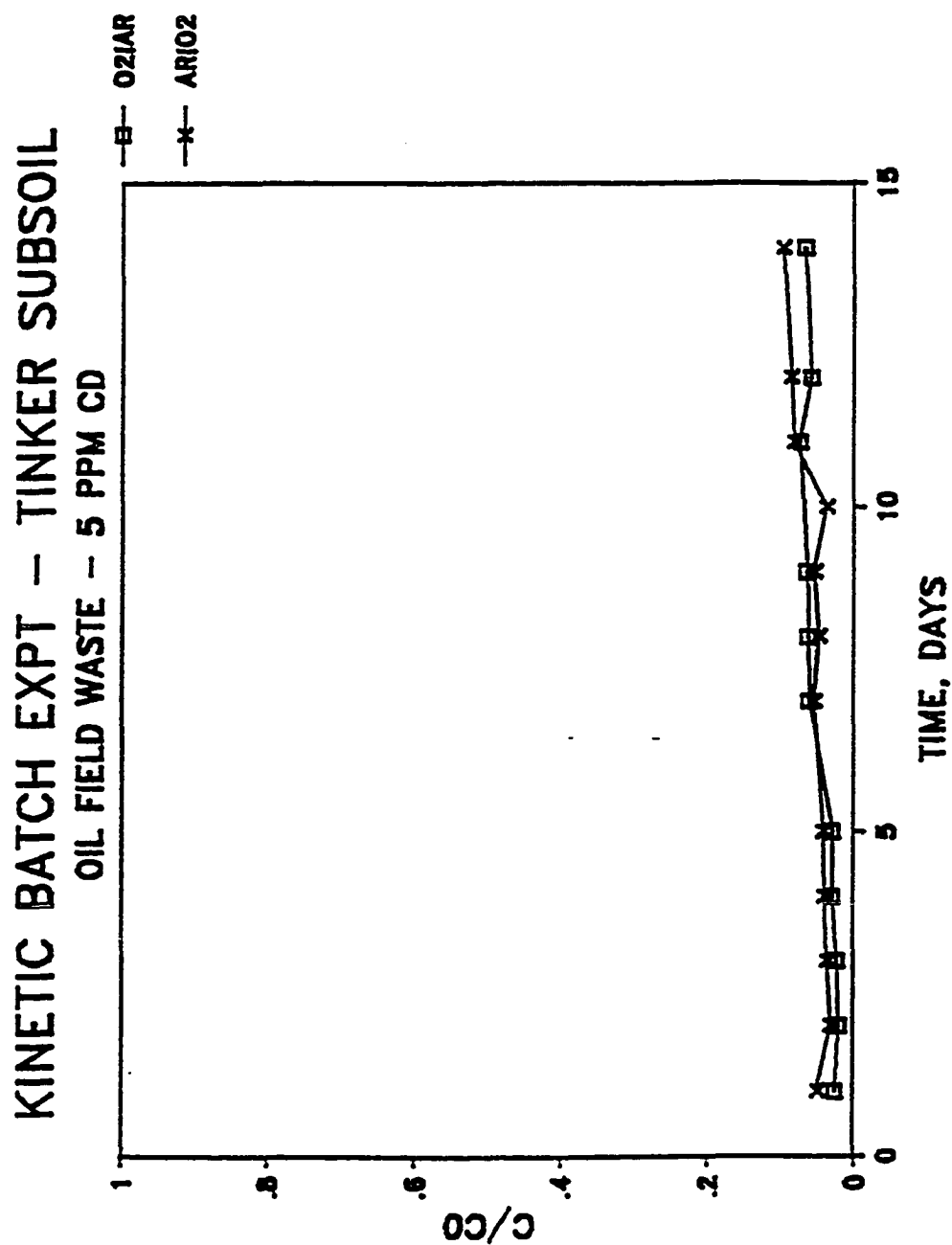


Figure 8. Retention of $5 \text{ mg} \cdot \text{L}^{-1}$ Cd in oil field waste by Tinker subsoil.

The acidic (pH 2) conditions and the presence of competing metals in the acidic metals waste led to very low retention of the Pb and Cd, usually less than half of the added metal, except for the Tinker soil where retention was usually greater than half, particularly for Pb. The high pH and CEC associated with the Tinker soil and the possible presence of carbonates were able to neutralize the acid in the waste. Huang et al. (1977) reported that for hydrous oxides and whole soils, retention followed the order: $\text{Cu(II)} > \text{Zn(II)} > \text{Pb(II)} > \text{Cd(II)}$. Therefore, Cu and Zn in the acidic metals waste may have been preferentially retained by these soils, reducing Cd and Pb retention.

Retention of Cd and Pb in the oil field waste (Figure 8) was less than in the $\text{Ca(NO}_3)_2$ solution (Figure 4) but greater than in the other two waste solutions (Figure 6 and 7). The organic constituent in the oil field waste was not present at high enough concentration to significantly prevent metal retention, nor were the other metals in this waste present at high enough concentrations to significantly compete for retention sites.

As part of this batch study, a treatment consisting of different purging gases (air or Ar) was included. Typically, those soil-suspensions purged first with air immobilized more metal than those first purged with Ar (Table 6). Though soil types, waste types, and time within purge treatments were pooled, these differences were significant, but generally the differences were not large. Thus, the small but significant differences in C/C_0 (equilibrated solution concentration vs. initial solution concentration) from the purge gas treatments should be used only as an indication that the redox effects likely influence metal retention in subsoils. Additional studies are needed to examine this effect.

Table 6. Effect of purging gas on metal retention.

Metal	Conc(mg•L ⁻¹)	Gas	Concentration, C/Co [†]
Cd	5	O ₂ [‡]	0.597 c [§]
		O ₂ /Ar	0.721 a
		Ar	0.699 b
		Ar/O ₂	0.683 b
	50	O ₂	0.690 c
		O ₂ /Ar	0.782 a
		Ar	0.795 a
		Ar/O ₂	0.751 b

Table 6. (Continued).

Metal	Conc(mg•L ⁻¹)	Gas	Concentration, C/Co [†]
Pb	50	O ₂	0.326 c
		O ₂ /Ar	0.380 a
		Ar	0.358 b
		Ar/O ₂	0.356 b
	500	O ₂	0.471 b
		O ₂ /Ar	0.550 a
		Ar	0.551 a
		Ar/O ₂	0.542 a

[†] C/Co pooled across soil type, waste type, and time.

[‡] O₂ = purged with O₂ for first 7 days

O₂/Ar = purged with Ar for second 7 days after purging with O₂

Ar = purged with Ar for first 7 days

Ar/O₂ = purged with O₂ for second 7 days after purging with Ar.

[§] Concentration values followed by the same letter within metal-level groups are not significantly different at the 0.05 level by the Duncan's Multiple Range Test.

In studies of redox potential effects on retention of Hg, Zn, Pb, and Cd in sediments, Gambrell et al. (1977) found that different processes seemed to be involved in controlling dissolved levels of these metals as concentrations increased from levels of a few $\text{mg}\cdot\text{kg}^{-1}$ to several hundred $\text{mg}\cdot\text{kg}^{-1}$ under oxidizing vs. reducing conditions at high metal concentrations in sediments. In sediments, a wider range of redox conditions affecting metal chemistry is possible compared to most subsoil materials. However, redox differences with depth do occur in subsoils and geologic materials though the range is often not as great as found in sediments. This relatively small range in redox potential in the subsoils subjected to different purging gases over this relatively short experimental period may have resulted in less of an oxidation/reduction effect than would be found under longer-term redox change conditions.

Sequential Fractionation of Retained Cd and Pb

Soil samples were obtained on Day 7 and 14 and extracted using a sequential fractionation scheme to determine selected chemical forms of retained Cd and Pb in the soil. Using the Pontchatoula subsoil and $\text{Ca}(\text{NO}_3)_2$ solution as an example, it can be observed that Cd (Figure 9) was more available (BaCl_2 exchangeable + EDTA extractable fractions) than Pb (Figure 10). Results of Khalid et al. (1979, 1981) and Gambrell et al. (1976, 1980) also indicated that Cd was retained in more available forms than was Pb. Exchangeable Cd was greater than exchangeable Pb. Very little Cd was retained by the oxide fractions. the oxide fractions were more important in Pb retention although only accounting for 5% - 30% of Pb retained. Similar trends over time, concentration, and purging gas can be observed for both Cd and Pb.

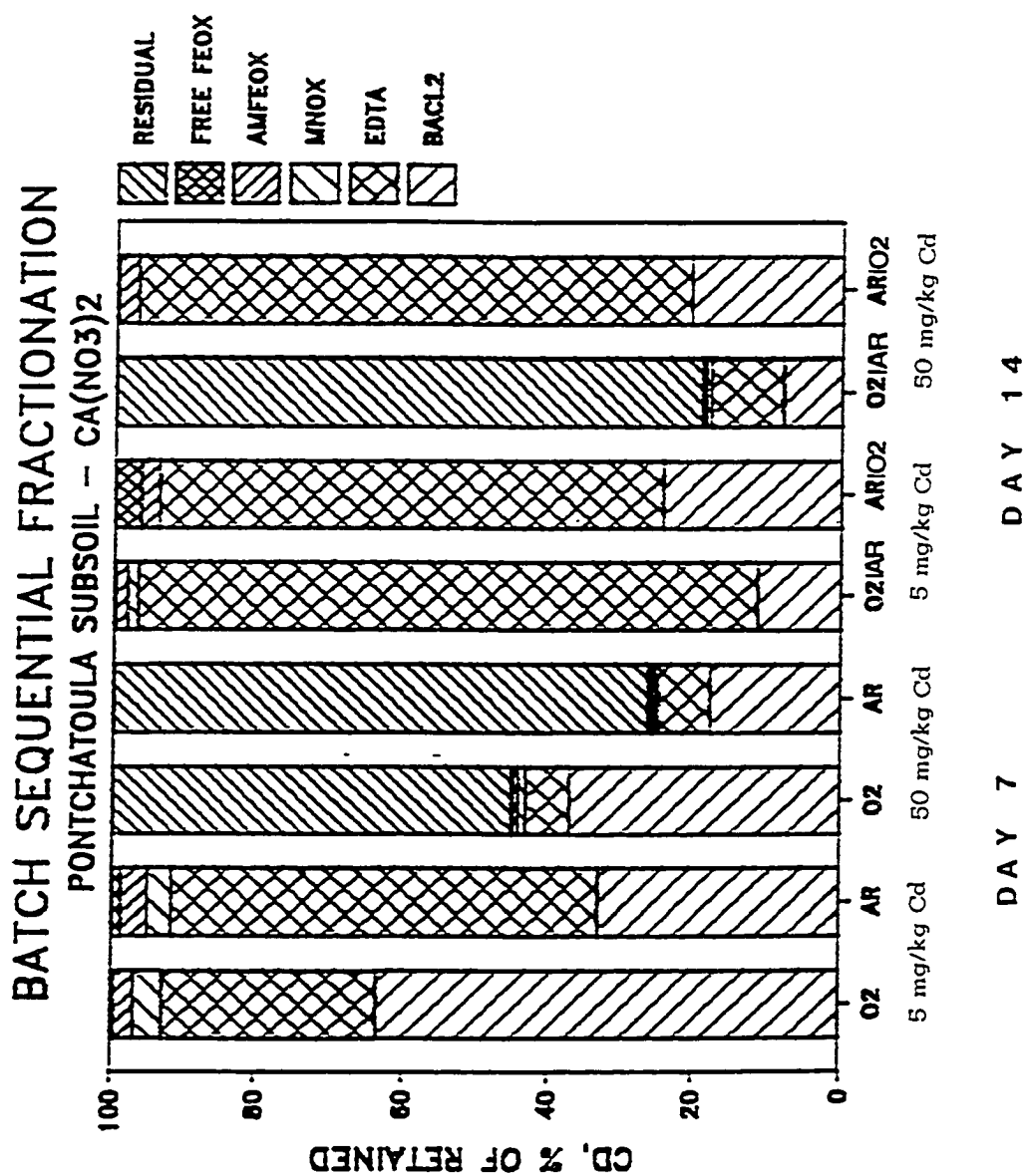


Figure 9. Fractionation of retained Cd in Pontchatoula subsoil for 0.005M $\text{Ca}(\text{NO}_3)_2$ solution.

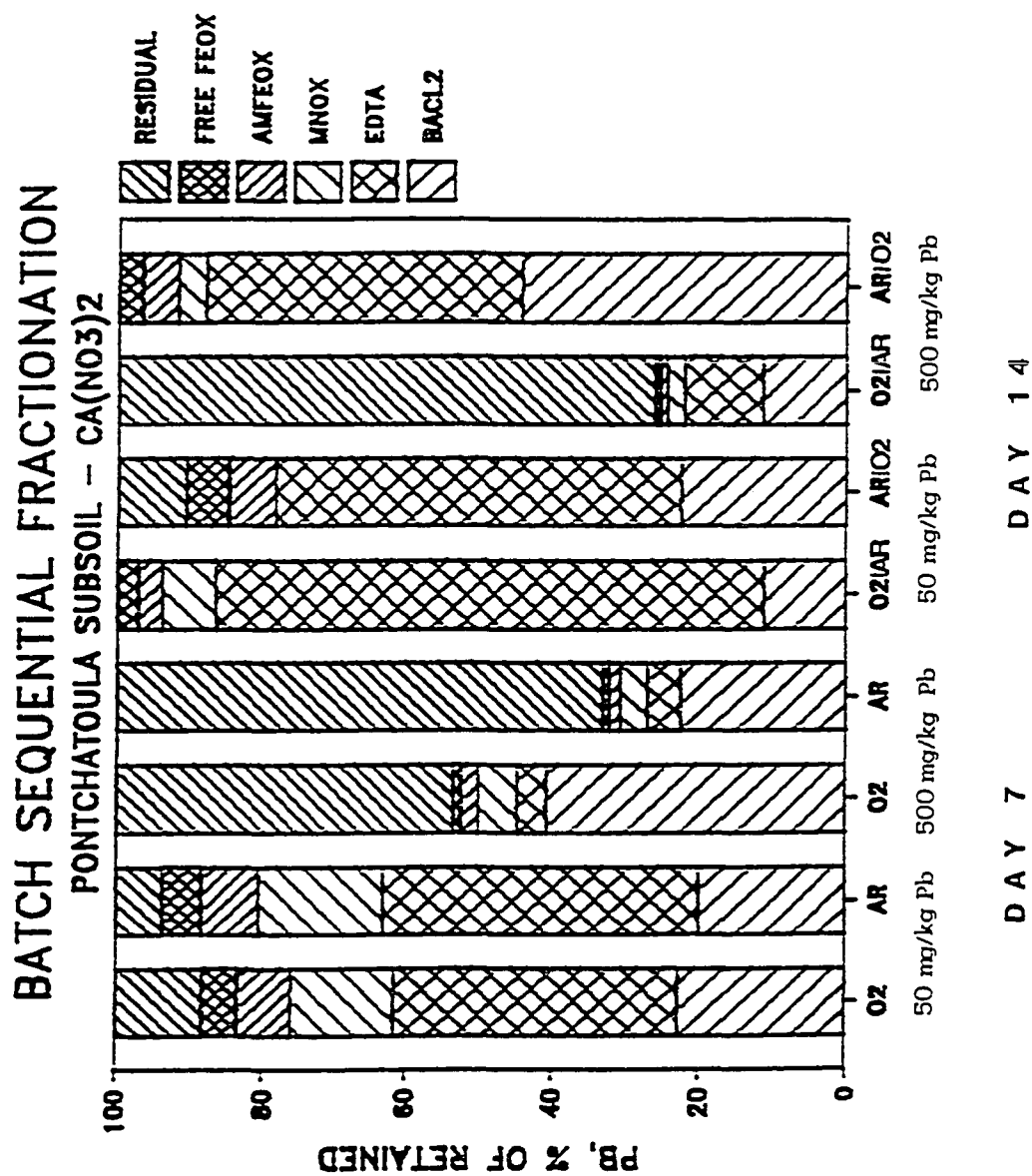


Figure 10. Fractionation of retained Pb in Pontchatoula subsoil for 0.005M $\text{Ca}(\text{NO}_3)_2$ solution.

Examining the effect of soil type on Pb fractionation, Pb was most available in the low pH, sandy Robins soil (Figure 11) and least available in the high pH, clayey Tinker soil (Figure 12), with the Pontchatoula soil intermediary (Figure 10). Gambrell et al. (1976, 1980) reported that the recovery of labelled Pb in the exchangeable fraction was influenced more by pH than oxidation intensity. This was also observed in this study. The differences between soils was greater than the differences between purge gases. Soil pH was the major factor controlling Cd and Pb retention in these soils (see Chapter 5).

The effect of solution composition on Pb fractionation is presented in Figures 10 and 13-15. Lead was fairly available in the $\text{Ca}(\text{NO}_3)_2$ solution (Figure 10). The EDTA-extractable Pb was greater at the lower concentration and increased with time.

Lead was very available in the synthetic leachate (Figure 13). Differences in Pb fractionation due to purging gas were observed in the leachate solution. The EDTA-extractable Pb was increased under Ar purging, indicating that Pb would be more available under reducing conditions. Lead in the EDTA-extractable fraction increased with time, as it did in the $\text{Ca}(\text{NO}_3)_2$ solution.

Lead was typically more available in the acidic metals waste (Figure 14). The BaCl_2 fraction was greater in this waste than in the others. The availability of Pb decreased over time.

For the oil field waste, differences were observed for the purging gases. Lead was more available under oxidizing conditions, opposite of the synthetic leachate. The increased availability under oxidizing conditions may have been due to the lower pH of the solution. Griffin and Shimp (1978) reported that as pH increased above pH 4, precipitation of

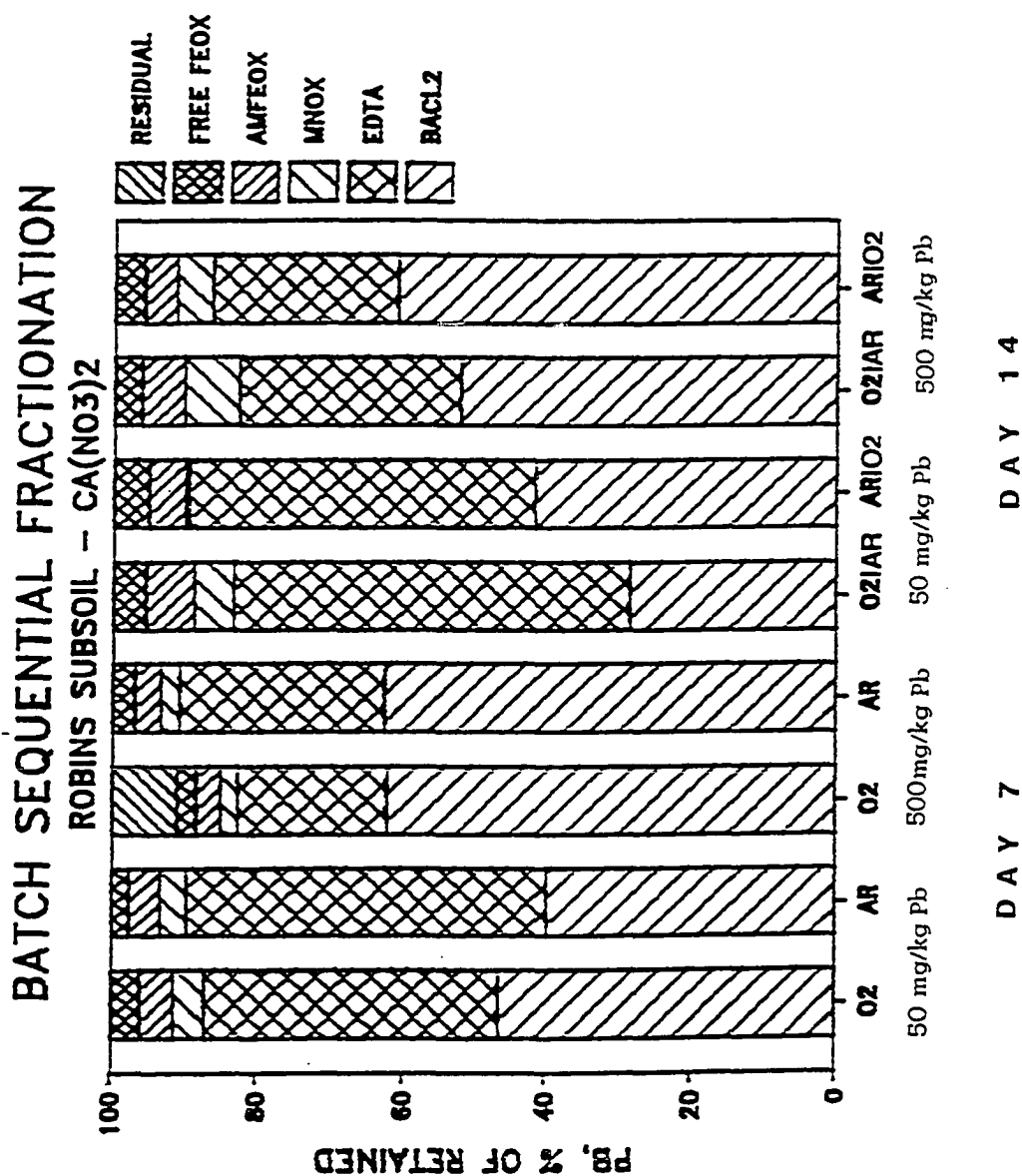


Figure 11. Fractionation of retained Pb in Robins subsoil for 0.005M $\text{Ca}(\text{NO}_3)_2$ solution.

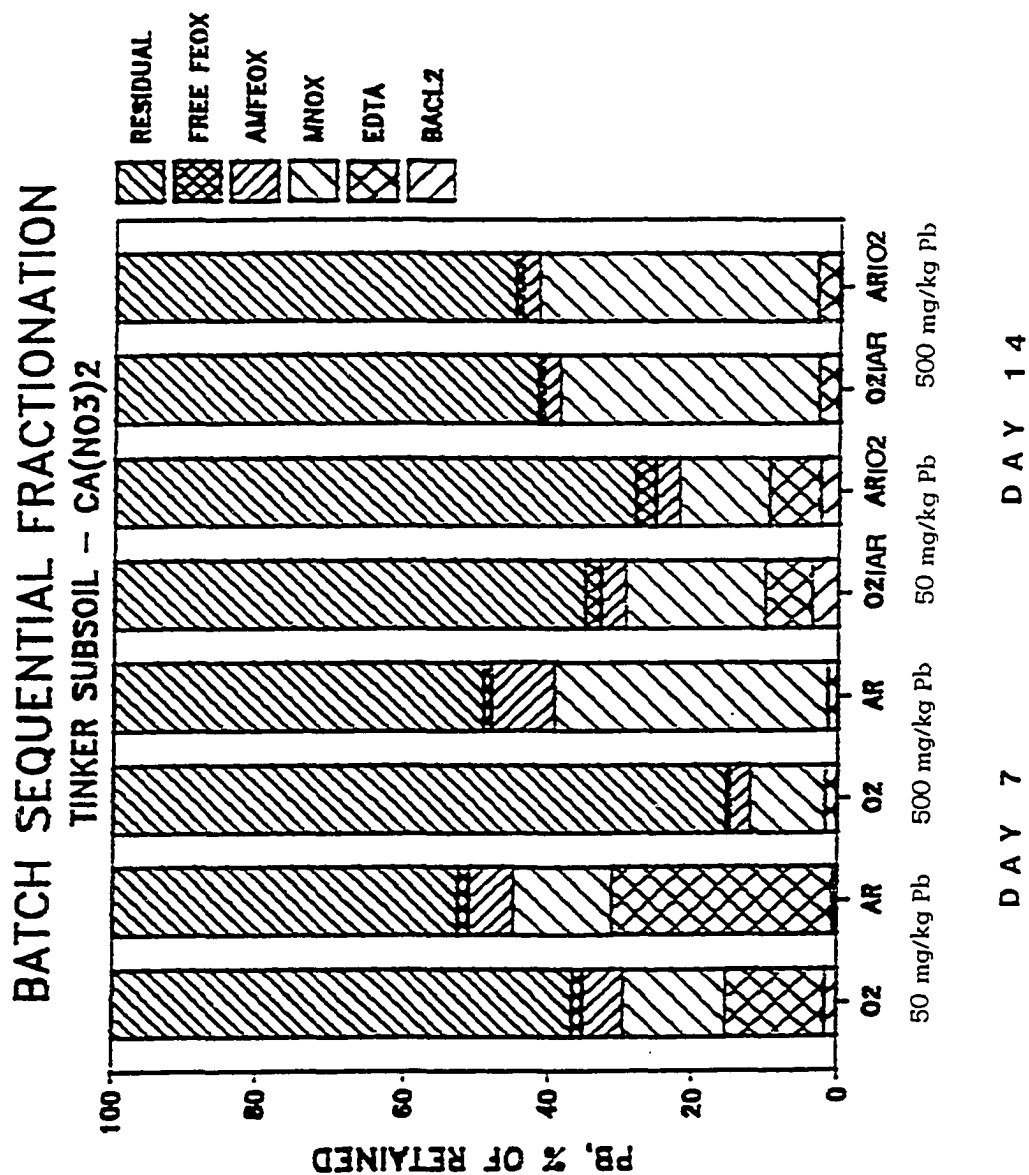


Figure 12. Fractionation of retained Pb in Tinker subsoil for 0.005M $\text{Ca}(\text{NO}_3)_2$ solution.

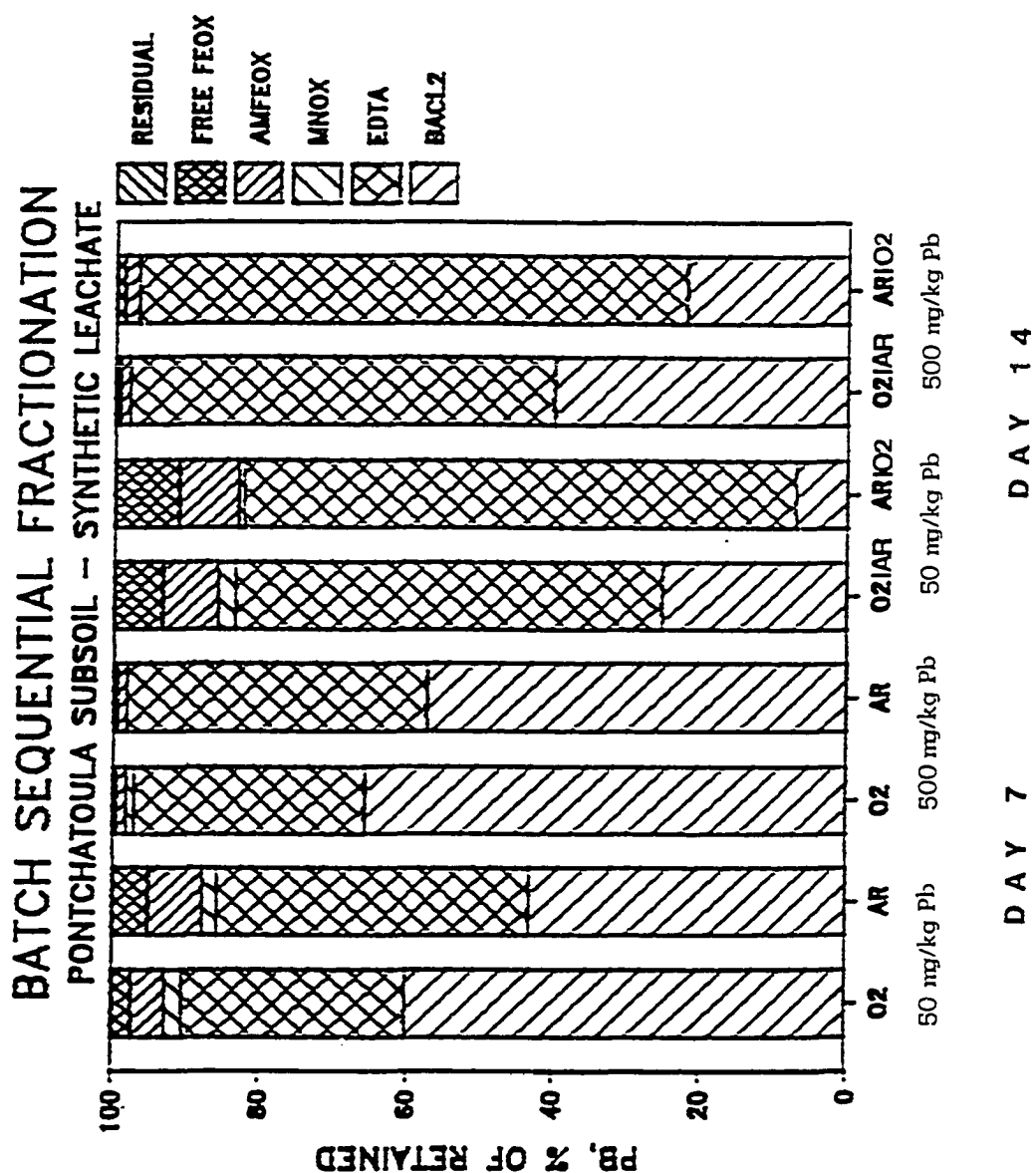


Figure 13. Fractionation of retained Pb in Pontchatoula subsoil for synthetic leachate solution.

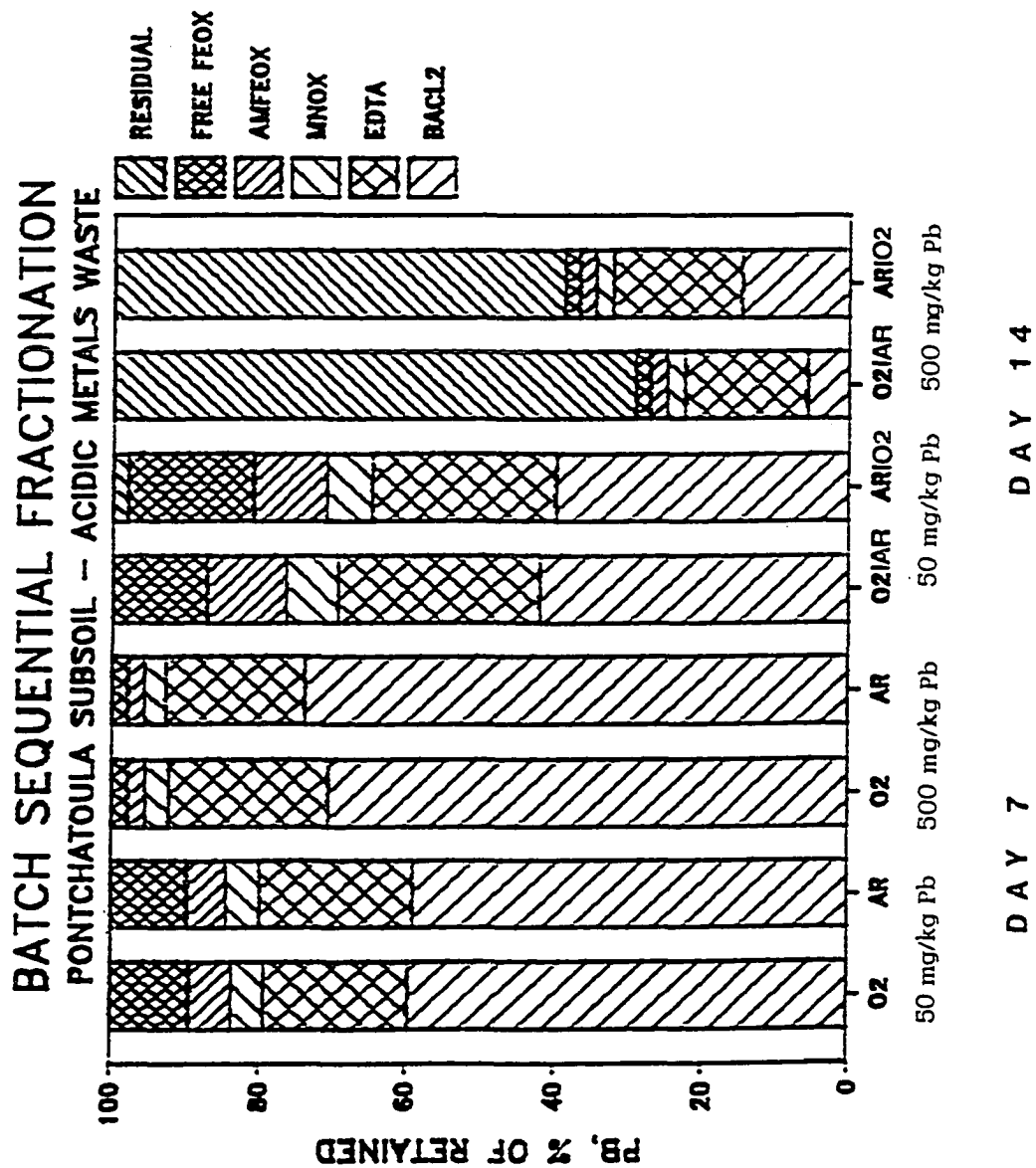
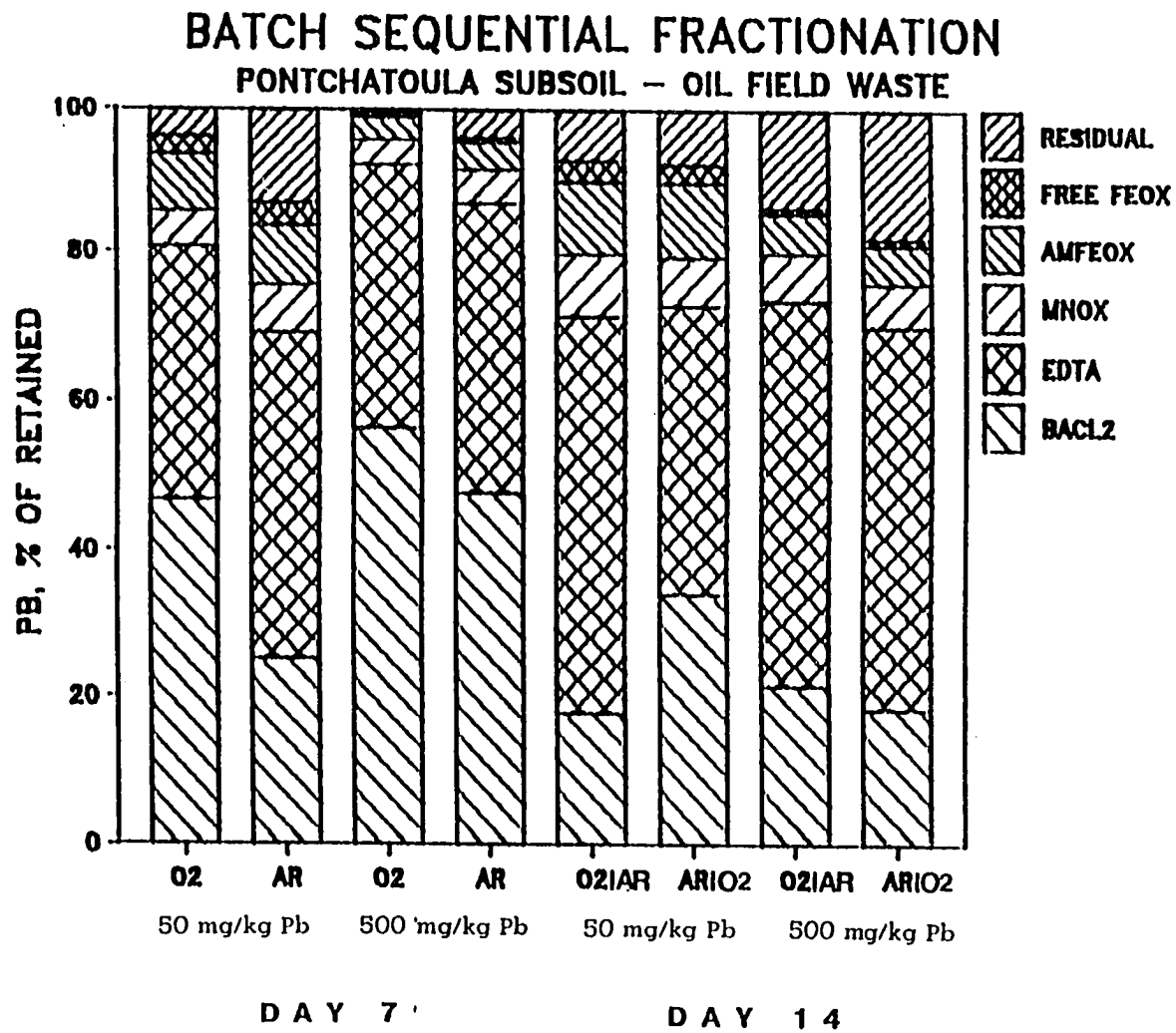


Figure 14. Fractionation of retained Pb in Pontchatoula subsoil for acidic metals waste.

Figure 15. Fractionation of retained Pb in Pontchatoula subsoil for oil field waste.



Cr(III) as an amorphous hydrated hydroxide occurred. Thus, as the soil solution was reduced, the pH increased causing the Cr(III) to precipitate, with the metals coprecipitating with the Cr(III), and therefore being rendered less available. This may have occurred in our study as well.

Gambrell et al. (1976, 1980) concluded that most of the labelled Pb and approximately half of the total indigenous Pb in sediment were recovered in potentially available forms under oxidizing conditions. Therefore, recent amendments did not allow Pb to react with soil minerals, leaving the Pb in available forms, as was observed in this study.

SUMMARY AND CONCLUSIONS

For all the soils and all the solutions, Pb was retained to a greater degree than was Cd. Retention of both metals followed the soils order: Tinker > Cecil \geq Pontchatoula \geq Combustion > Robins; that is greatest retention in the soil with the highest pH, clay content, CEC, and Fe oxide content. At the lower concentrations of Pb and Cd, greater proportions of the metals were retained by the soil. Metal removal from the four solutions decreased in the order: $\text{Ca}(\text{NO}_3)_2$ > oil field > acidic metals \geq synthetic leachate. Typically, those soil-suspensions purged with O_2 immobilized more metal than those purged with Ar.

The sequential fractionation studies indicated that Cd was retained in more available forms than was Pb. Lead was most available in the Robins soil and least available in the Tinker soil. Solution composition did affect availability of retained Pb.

Working with uncontaminated soils, this batch study demonstrated:
(1) the different soil types have very different capacities for

immobilizing metals, (2) the potential for metals release and transport increases with increasing metal levels present, and (3) the presence of additional waste materials other than metals can greatly reduce a soil's ability to retain metals.

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CHAPTER 7

THE EFFECT OF SOLUTION COMPOSITION ON THE
TRANSPORT OF CADMIUM AND LEAD IN SUBSOILS

ABSTRACT

This study was undertaken to determine the effects of soil physical and chemical properties and especially the effect of the concentration of solute and the composition of the waste solution on the transport of Pb and Cd through packed columns of subsoil materials. Two soils with different properties were used as well as four synthetic solutions, three of which represent various types of waste solutions. These solutions were: 0.005M $\text{Ca}(\text{NO}_3)_2$, municipal landfill leachate, acidic metals waste, and oil field waste.

The sandy Norfolk soil had a low retention capacity, and thus breakthrough occurred early in this soil. Breakthrough of Cd occurred prior to Pb for both soils and all solutions. Breakthrough of higher concentrations of Cd and Pb was faster than at lower concentrations for all solutions. For the different waste solutions, breakthrough occurred in the order: acidic metals waste > synthetic leachate > 0.005M $\text{Ca}(\text{NO}_3)_2$ > oil field waste. There appeared to be two species of Pb and Cd in the synthetic leachate during transport through the Norfolk soil.

INTRODUCTION

The transport of metals to groundwater below hazardous waste sites is an environmental concern (Nelson, 1983). The movement of the metals is determined by the soil's chemical and physical properties, the concentration of the solute, and the composition of the waste solution (LaBauve et al., 1988). The soil properties affecting metal retention/release and transport include bulk density, surface area, particle-size distribution, pH, redox status, ion exchange capacity, amount of organic matter, type and amount of metal oxides, and type and amount of clay minerals (Amacher et al., 1986).

In a hazardous waste dump or landfill, a variety of types of waste may be present that may become mixed with metals at or beneath the site. Mixtures of metals and other wastes may interact to influence metal mobilization/immobilization. The presence of toxic metals with acidic wastes, for example, would greatly enhance the leaching of metals beneath the initial disposal zone toward groundwater. This is a set of parameters that has not been thoroughly addressed in the toxic metals studies associated with sludge-amended soils or contaminated sediments as very acidic conditions are rarely encountered in these situations. Also, certain organic wastes in high concentration may affect the mobility of metals. It is likely that there are many locations where waste mixtures are present that may enhance or have already enhanced the leaching of metals to groundwater.

The objectives of this study were to analyze the effects of soil type, solute concentration, and waste solution composition on the

transport of Cd and Pb through packed columns of subsoil material under saturated flow conditions.

MATERIALS AND METHODS

Soil Selection and Characterization

Uncontaminated subsoil materials were collected from Robins AFB in Warner Robins, Ga. (Norfolk subsoil) and from the South Carolina Simpson Agricultural Experiment Station near Clemson, South Carolina (Cecil subsoil). The taxonomic classification of the two soils is given in Table 1. Selected chemical and physical characteristics of the soils are presented in Table 2. The pH of the samples was determined in a 1:1 soil:water paste (McLean, 1982). Cation exchange capacity (CEC) was determined by summing the major cations (Ca, Mg, Na, K, and Al) extracted with 0.1M BaCl₂ (adapted from Rhoades, 1982). Particle-size distribution was determined by the hydrometer method (Gee and Bauder, 1986). The Mn oxide content of the samples was extracted using pH 2, 0.1M hydroxylamine hydrochloride (NH₂OH•HCl) (Chao, 1972). Amorphous Fe oxides were determined using 0.25M hydroxylamine hydrochloride-0.25M HCl (Chao and Zhou, 1983). Free Fe oxides were determined using the dithionite-citrate-bicarbonate method (DCB) (Mehra and Jackson, 1960). These two soil materials were selected because of their different textures (sand, silt, and clay content) and hydrous oxide contents.

Experimental Procedure

The subsoil material was air-dried and ground to pass a 2-mm sieve prior to use. The solutions used in this study are listed in Table 3.

Table 1. Classification of soil materials.

Soil Series	Taxonomic Classification
Cecil	clayey, kaolinitic, thermic, Typic Hapludult
Norfolk	fine-loamy, siliceous, thermic, Typic Paleudult

Table 2. Selected chemical and physical properties of soils used in column study.

Soil	pH	CEC	MnO ₂	Amorph. Total		Sand	Silt	Clay
				Fe ₂ O ₃	Fe ₂ O ₃			
		cmol(+)/kg	-----	-----	%	-----	-----	-----
Cecil	4.92	2.58	0.005	0.051	1.030	18	9	73
Norfolk	3.50	1.31	0.001	0.014	0.059	72	13	15

Table 3. Composition of synthetic soil and waste solutions used in column study.

Waste Solution	Composition
$\text{Ca}(\text{NO}_3)_2^{\dagger}$	0.005M $\text{Ca}(\text{NO}_3)_2$
Synthetic Municipal Landfill	0.15M sodium acetate
Leachate (Aerobic) [‡]	0.15M acetic acid
	0.050M glycine
	0.007M salicylic acid
Acidic Metals Waste	100 $\text{mg}\cdot\text{L}^{-1}$ Cu 200 $\text{mg}\cdot\text{L}^{-1}$ Ni
	200 $\text{mg}\cdot\text{L}^{-1}$ Cr 300 $\text{mg}\cdot\text{L}^{-1}$ Zn
	HCl to pH 2
Oil Field Waste [§]	50 $\text{mg}\cdot\text{L}^{-1}$ Ba 10 $\text{mg}\cdot\text{L}^{-1}$ Cr(III)
	25 $\text{mg}\cdot\text{L}^{-1}$ naphthalene

Each solution also contained either:

- (a) 500 $\text{mg}\cdot\text{L}^{-1}$ Pb + 50 $\text{mg}\cdot\text{L}^{-1}$ Cd, or
- (b) 50 $\text{mg}\cdot\text{L}^{-1}$ Pb + 5 $\text{mg}\cdot\text{L}^{-1}$ Cd

[†]Amacher et al., 1986.

[‡]Stanforth et al., 1979.

[§]Pardue (unpubl.).

The soils were packed to a bulk density of approximately 1.3 into 4.5 cm x 10 cm plexiglass columns, as illustrated in Figure 1. The soils were saturated with 0.005M $\text{Ca}(\text{NO}_3)_2$, simulating a soil solution (Amacher et al., 1986). The metal waste solutions or the $\text{Ca}(\text{NO}_3)_2$ solution were then passed through the columns under saturated flow conditions at a flow rate of approximately $1.8 \text{ cm} \cdot \text{hr}^{-1}$ for 4 to 5 pore volumes. The columns were then leached to desorb the metals from the soils using up to 20 pore volumes of 0.005M $\text{Ca}(\text{NO}_3)_2$. Effluent was collected at 0.1 pore volume increments, starting when the metal solutions were added. The effluent was analyzed by ICP for the metals of interest. Column parameters are listed in Table 4. Pore water velocity is equal to the water flux divided by the water content. The column retention time is the column length divided by the pore water velocity. The pulse volume is the volume of waste solution added as a pulse to the soil column.

Breakthrough curves (BTC) for the metals leached through the soil columns were obtained from the data by plotting the concentration of the effluent divided by the initial concentration (C/C_0) versus pore volume. The retardation factor (R) was determined experimentally from the effluent side of the BTC's by determining the pore volume at the half-height of the BTC (van Genuchten and Wierenga, 1986). The distribution ratio (K_d), the ratio of concentration of metal sorbed to the concentration in solution, was determined from the equation, $R = 1 + \rho K_d / \theta$, where R is the retardation factor, ρ is the soil bulk density ($\text{g} \cdot \text{cm}^{-3}$), K_d is the distribution ratio ($\text{cm}^3 \cdot \text{g}^{-1}$), and θ is the water content ($\text{cm}^3 \cdot \text{cm}^{-1}$) (van Genuchten and Wierenga, 1986). The percent recovery was estimated using a grid system.

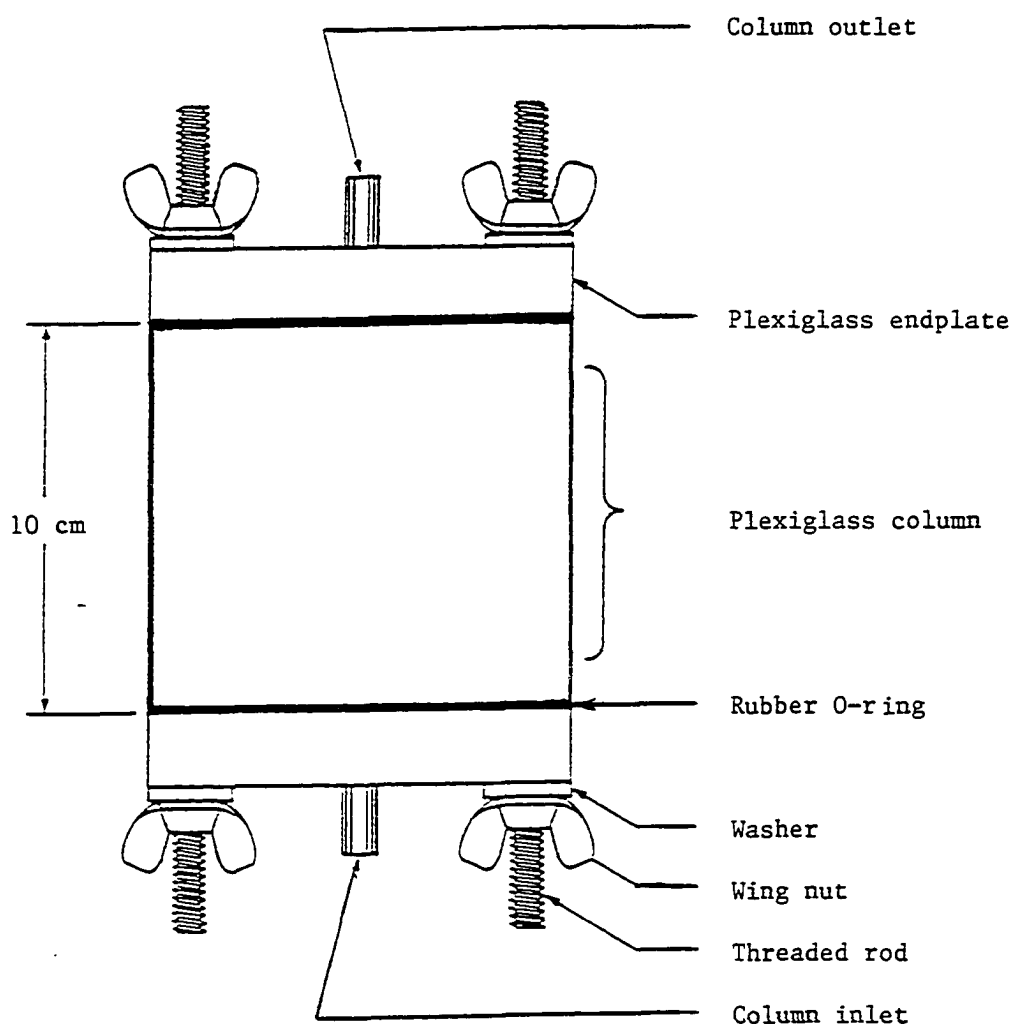


Figure 1. Diagram of column used in column transport studies.

Table 4. Column parameters used in this study.

Soil, Solution, and Concentration of Metal	soil bulk density ($\text{g}\cdot\text{cm}^{-3}$)	pore volume (cm^3)	water content ($\text{cm}^3\cdot\text{cm}^{-3}$)	water flux --- ($\text{cm}\cdot\text{hr}^{-1}$) ---	pore water velocity --- ($\text{cm}\cdot\text{hr}^{-1}$) ---	residence time (hr)	pulse volume (cm^3)
Cecil							
$\text{Ca}(\text{NO}_3)_2$ -50 Pb/5 Cd	1.06	100.35	0.600	1.97	3.28	3.05	480
-500 Pb/50 Cd	1.06	100.35	0.600	1.92	3.20	3.12	450
Syn Leach -50 Pb/5 Cd	1.02	103.13	0.617	1.84	2.98	3.36	467
-500 Pb/50 Cd	1.02	103.13	0.617	1.92	3.11	3.21	460
Acidic Metals -50 Pb/5 Cd	1.02	102.75	0.614	1.70	2.77	3.61	425
-500 Pb/50 Cd	1.02	102.75	0.614	1.71	2.78	3.60	425
Oil Field -50 Pb/5 Cd	1.01	103.67	0.620	1.89	3.05	3.28	500
-500 Pb/50 Cd	1.01	103.67	0.620	1.88	3.03	3.30	500

Table 4. (Continued).

Soil, Solution, and Concentration of Metal	soil bulk density ($\text{g}\cdot\text{cm}^{-3}$)	pore volume (cm^3)	water content ($\text{cm}^3\cdot\text{cm}^{-3}$)	water flux ---- ($\text{cm}\cdot\text{hr}^{-1}$)	pore water velocity ---- ($\text{cm}\cdot\text{hr}^{-1}$)	residence time (hr)	pulse volume (cm^3)
Norfolk							
$\text{Ca}(\text{NO}_3)_2$ -50 Pb/5 Cd	1.32	83.94	0.502	1.60	3.19	3.13	380
-500 Pb/50 Cd	1.32	83.94	0.502	1.79	3.57	2.80	425
Syn Leach -50 Pb/5 Cd	1.34	82.73	0.495	1.83	3.70	2.70	300
-500 Pb/50 Cd	1.34	82.73	0.495	1.79	3.62	2.76	285
Acidic Metals -50 Pb/5 Cd	1.34	82.37	0.465	1.81	3.89	2.57	432
-500 Pb/50 Cd	1.34	82.37	0.465	1.87	4.02	2.49	458
Oil Field -50 Pb/5 Cd	1.51	72.14	0.431	1.78	4.13	2.42	240
-500 Pb/50 Cd	1.51	72.14	0.431	1.76	4.08	2.45	270

RESULTS AND DISCUSSION

Miscible displacement studies were performed with two soils (the Cecil soil and the Norfolk soil from Robins AFB), two metals each at two solute concentrations ($5 \text{ mg}\cdot\text{L}^{-1}$ Cd plus $50 \text{ mg}\cdot\text{L}^{-1}$ Pb and $50 \text{ mg}\cdot\text{L}^{-1}$ Cd plus $500 \text{ mg}\cdot\text{L}^{-1}$ Pb) and three synthetic waste solutions (synthetic municipal landfill leachate, synthetic acidic metals waste, and a simulated oil field waste) plus $\text{Ca}(\text{NO}_3)_2$. The Norfolk soil retained less metals than the Cecil soil, and therefore breakthrough typically occurred at lower pore volumes (Figures 2-9; Table 5). The Norfolk soil is sandier, and has a lower pH, CEC, and metal oxides content than the Cecil soil, all of which probably contributed to the lower retention capacity of the Norfolk soil. Soil type did not substantially influence the breakthrough time for the acidic metals waste, particularly for Cd (Table 5). Whereas no Pb peak was observed at $50 \text{ mg}\cdot\text{L}^{-1}$ Pb (+ $5 \text{ mg}\cdot\text{L}^{-1}$ Cd) in the simulated oil field waste in the Cecil soil (Figure 4), the oil field waste facilitated movement of Pb through the Norfolk soil (Figure 8). The opposite soil effect was observed for the synthetic leachate medium (Figures 4 and 8).

Breakthrough of Cd occurred prior to that of Pb for both soils and all solutions (Figures 2-9; Table 5). At low concentrations of Pb with $\text{Ca}(\text{NO}_3)_2$ instead of a co-waste, breakthrough of Pb occurred. Breakthrough at higher concentrations of Cd and Pb was faster than at lower concentrations for all solutions, indicating the importance of metal concentration on the potential for metal movement. Higher concentrations of metals apparently overwhelm the capacity of various metal retention mechanisms in these soils (Fuller, 1980).

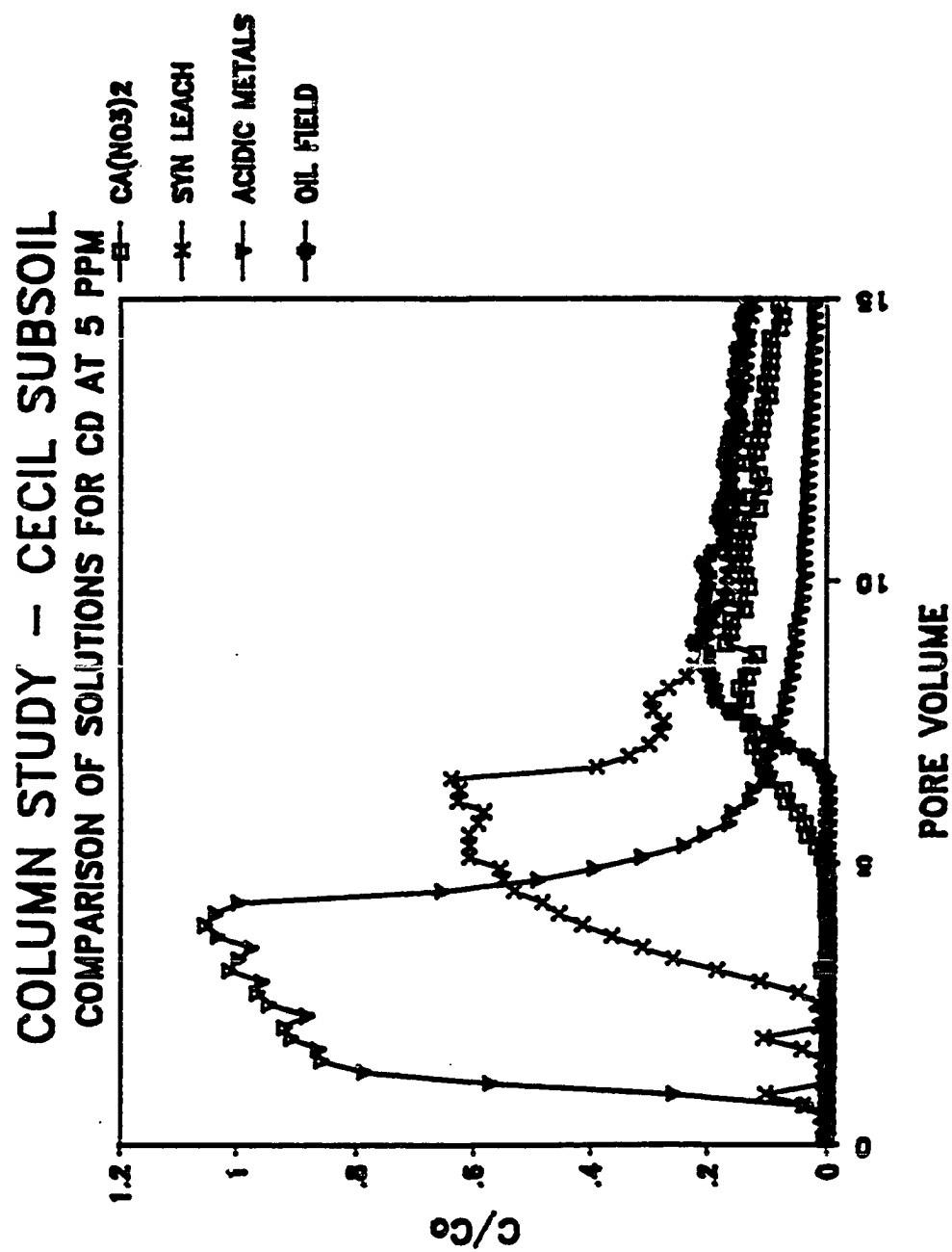


Figure 2. Comparison of waste solutions for Cd at $5 \text{ mg} \cdot \text{L}^{-1}$ for the Cecil subsoil.

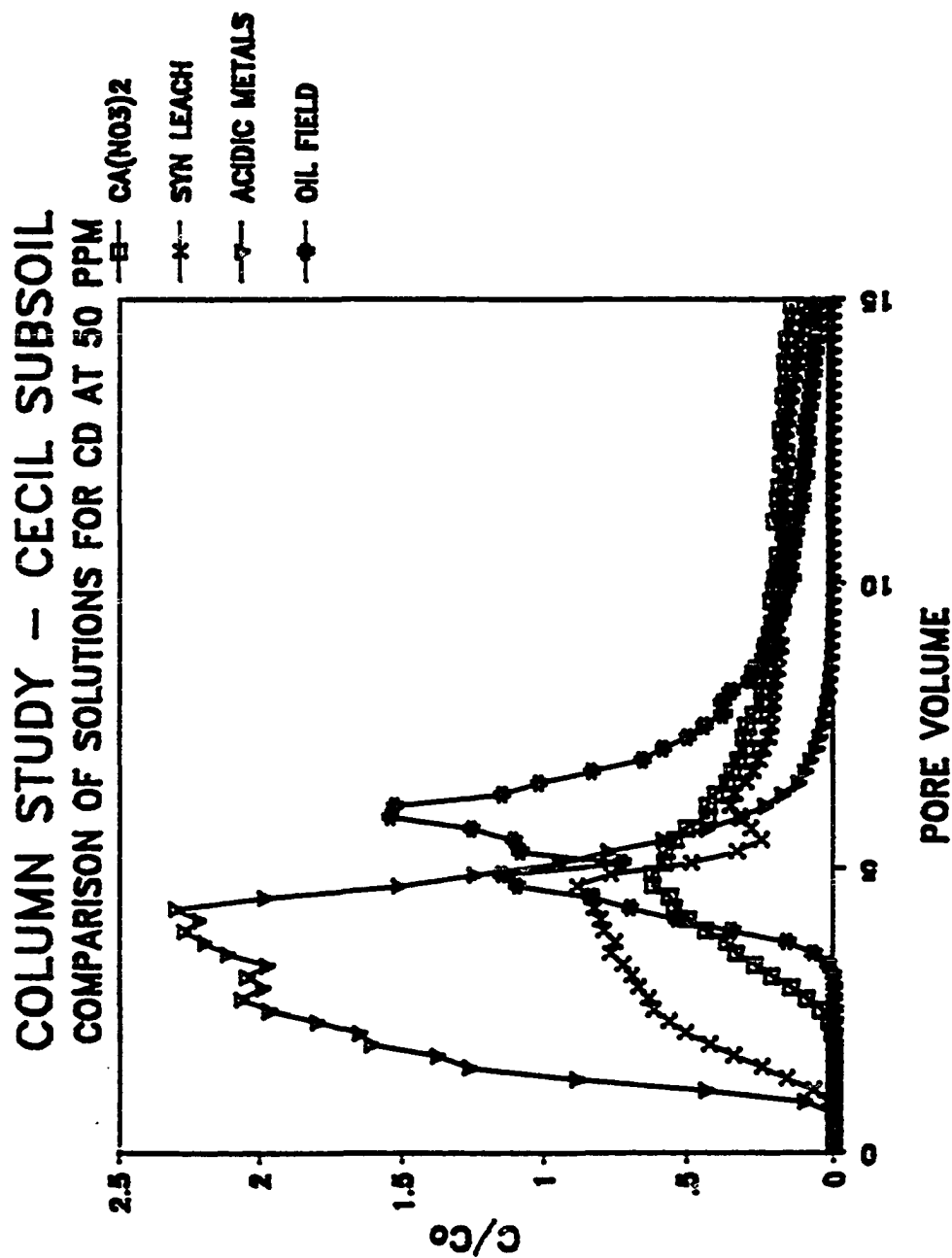


Figure 3. Comparison of waste solutions for Cd at 50 mg·L⁻¹ for the Cecil subsoil.

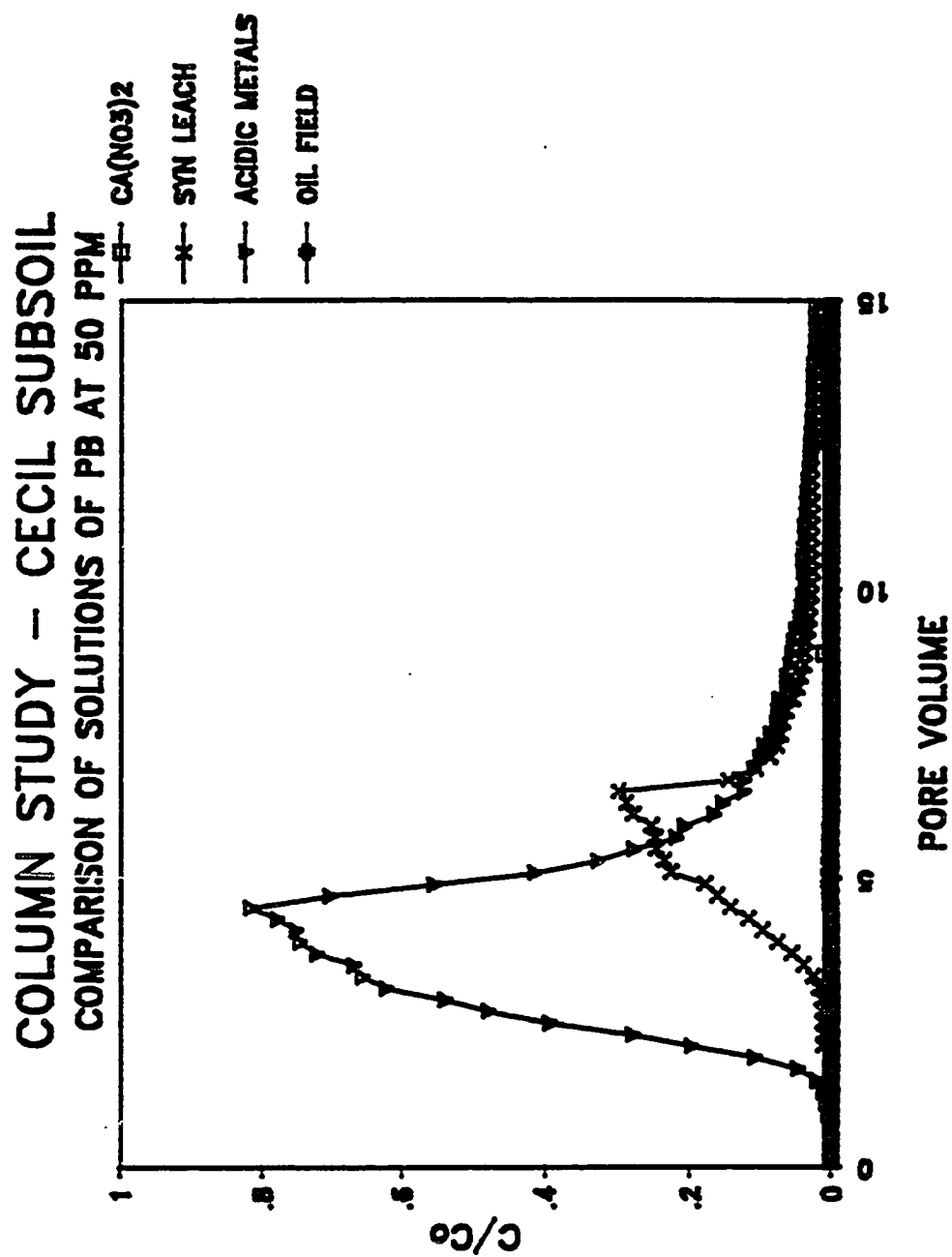


Figure 4. Comparison of waste solutions for Pb at $50 \text{ mg} \cdot \text{L}^{-1}$ for the Cecil subsoil.

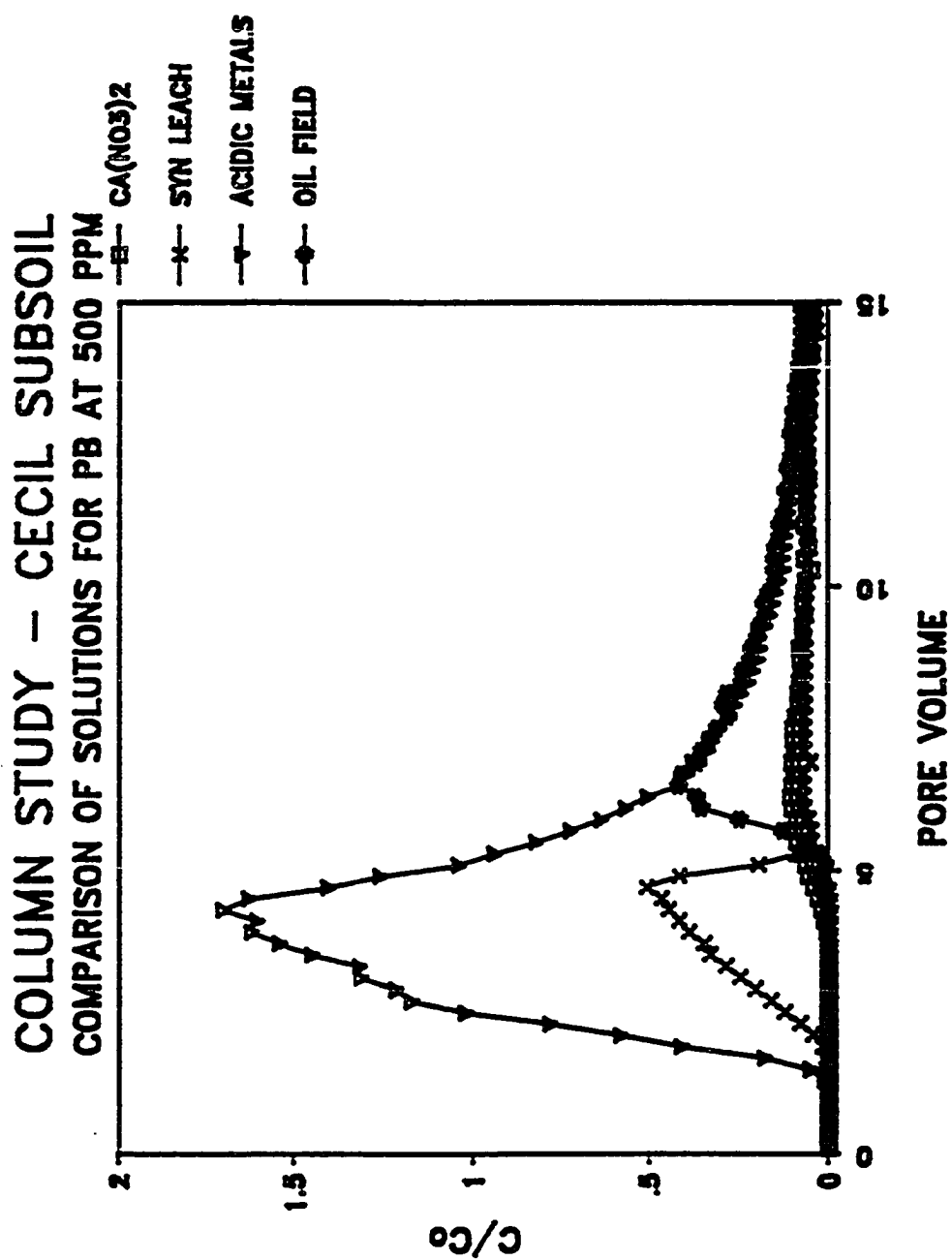


Figure 5. Comparison of waste solutions for Pb at $500 \text{ mg}\cdot\text{L}^{-1}$ for the Cecil subsoil.

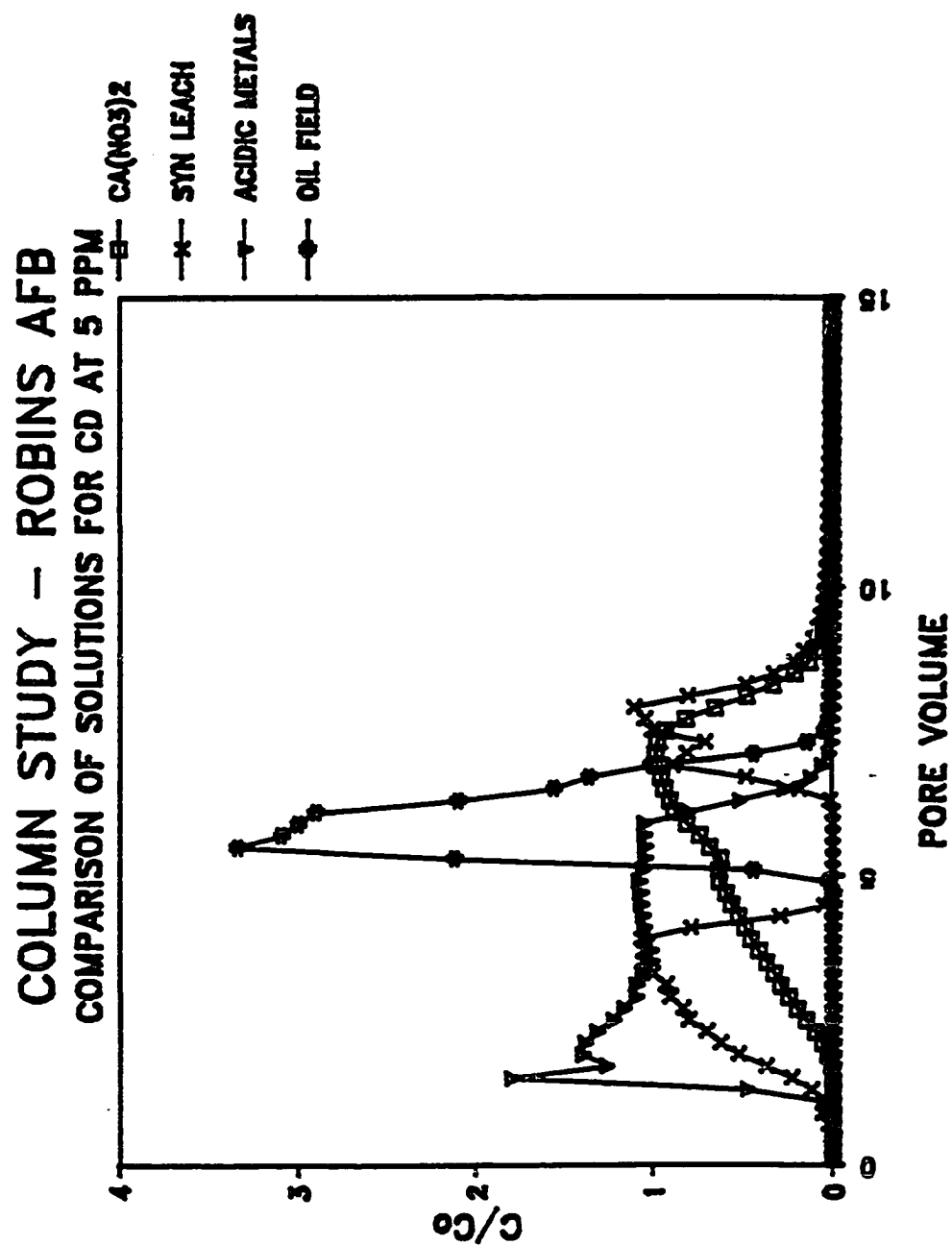


Figure 6. Comparison of waste solutions for Cd at $5 \text{ mg} \cdot \text{L}^{-1}$ for the Norfolk subsoil.

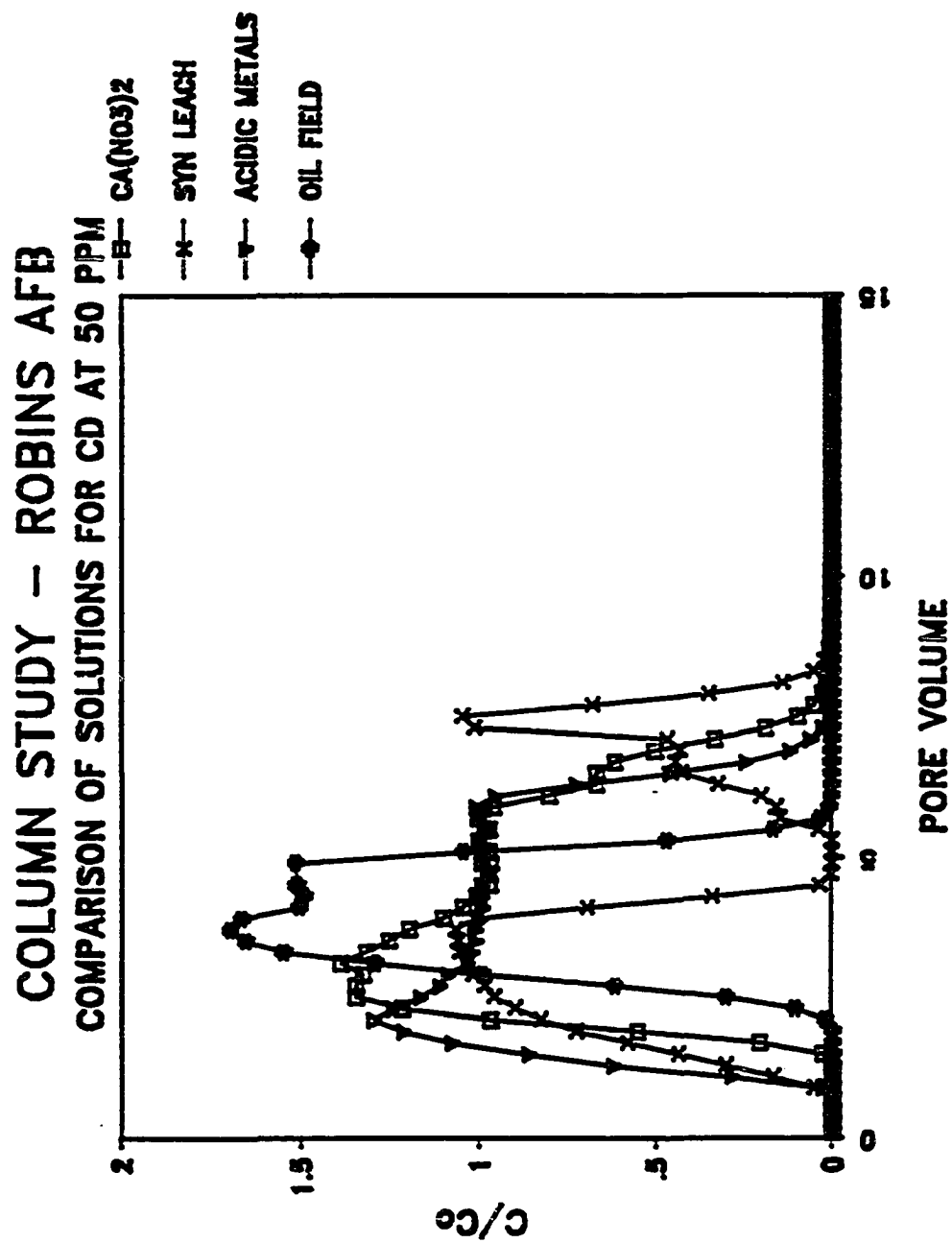


Figure 7. Comparison of waste solutions for Cd at $50 \text{ mg} \cdot \text{L}^{-1}$ for the Norfolk subsoil.

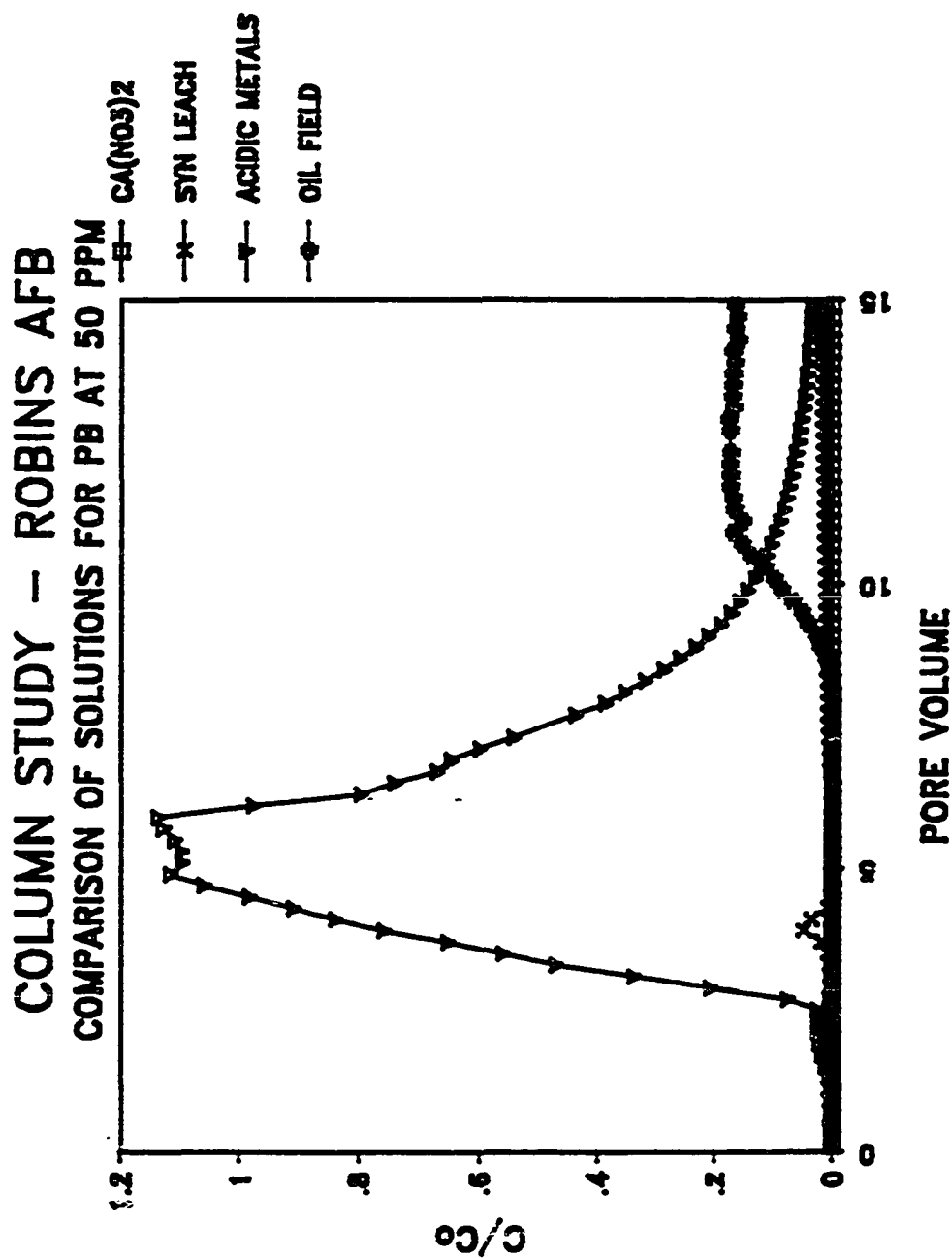


Figure 8. Comparison of waste solutions for Pb at $50 \text{ mg}\cdot\text{L}^{-1}$ for the Norfolk subsoil.

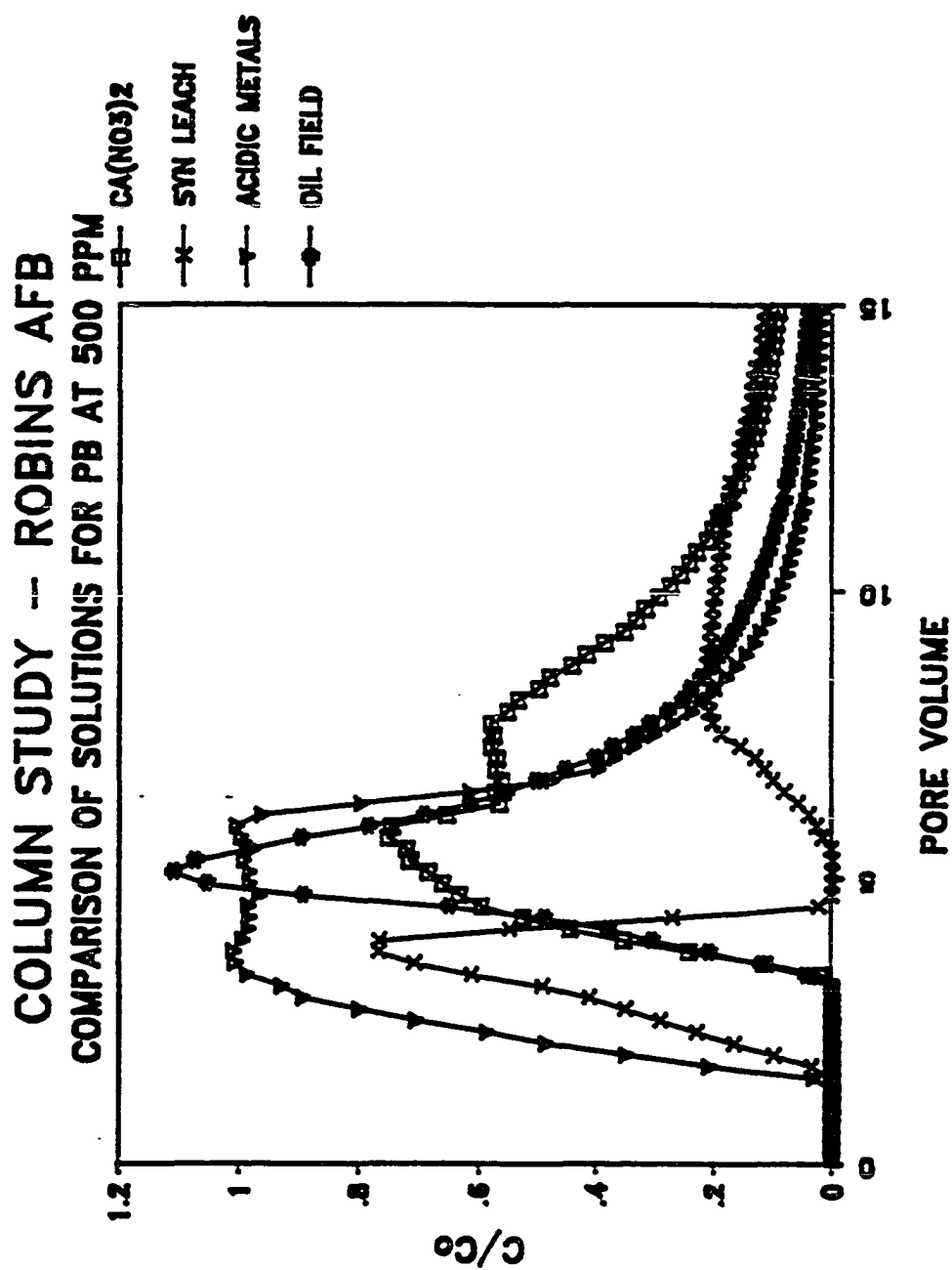


Figure 9. Comparison of waste solutions for Pb at $500 \text{ mg} \cdot \text{L}^{-1}$ for the Norfolk subsoil.

Table 5. Experimentally measured retardation factor (R) from effluent side of the BTC's.
 K_p values were calculated using $R = 1 + \rho K_p / \theta$.

Soil, Solution, and Concentration of Metal	R		K_p (cm·g ⁻¹)		% Recovery		Tailing	
	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb
Cecil								
Ca(NO ₃) ₂ -50 Pb/5 Cd	6.4	-	2.05	-	25	0	Yes	Yes
-500 Pb/50 Cd	3.4	4.9	0.91	1.48	83	27	Yes	Yes
Syn Leach -50 Pb/5 Cd	3.5	4.4	0.92	1.25	78	23	Yes	Yes
-500 Pb/50 Cd	2.0	3.2	0.37	0.81	98	35	Yes	Yes
Acidic Metals -50 Pb/5 Cd	1.1	2.6	0.04	0.59	99	57	Yes	Yes
-500 Pb/50 Cd	1.4	2.4	0.15	0.51	100	100	No	No
Oil Field -50 Pb/5 Cd	7.4	-	1.83	-	32	0	Yes	Yes
-500 Pb/50 Cd	5.2	5.8	1.20	1.37	98	44	Yes	Yes

Table 5. (Continued).

Soil, Solution, and Concentration of Metal	R		$K_d (\text{cm} \cdot \text{g}^{-1})$		% Recovery		Tailing	
	Cd	Pb	Cd	Pb	Cd	Pb	Cd	Pb
Norfolk								
Ca(NO ₃) ₂ -50 Pb/5 Cd	4.2	-	1.81	-	100	0	No	Yes
-500 Pb/50 Cd	2.0	4.0	0.57	1.70	100	80	No	Yes
Syn Leach -50 Pb/5 Cd	2.0, 6.8	-	0.61, 3.52	- , -	100	1	No	Yes
-500 Pb/50 Cd	1.6, 7.2	2.8, 6.8	0.36, 3.76	1.09, 3.52	100	71	No	Yes
Acidic Metals -50 Pb/5 Cd	1.4	3.5	0.24	1.50	100	92	No	Yes
-500 Pb/50 Cd	1.4	2.2	0.24	0.72	100	99	No	Yes
Oil Field -50 Pb/5 Cd	5.2	10.0	2.58	5.54	100	26	No	Yes
-500 Pb/50 Cd	2.8	4.4	1.11	2.09	100	84	No	Yes

Comparing solutions, breakthrough occurred in the order: acidic metals waste > synthetic leachate > 0.005M $\text{Ca}(\text{NO}_3)_2$ > oil field waste (Table 5). This indicates that Cd and Pb in the acidic metals waste were retained the least by the soils, while Cd and Pb in the oil field waste were retained the most by the soils.

The lack of retention of Cd and Pb in the acidic metals waste was due to the low pH (pH2) of the waste and competition with other metals in the waste. Huang et al. (1977) reported that for hydrous oxides and whole soils, retention followed the order: $\text{Cu(II)} > \text{Zn(II)} > \text{Pb(II)} > \text{Cd(II)}$. Therefore, Cu and Zn may have been preferentially retained by the soil, thus increasing Pb and Cd mobility in the soil. For the synthetic acidic metals waste, breakthrough occurred in the following order: $\text{Cd} \geq \text{Ni} \geq \text{Zn} > \text{Cu} > \text{Pb} > \text{Cr}$, although Cu breakthrough was very close to that of Cd, Ni, and Zn (Figure 10). Therefore, Cu, Zn, and Ni were preferentially retained over Cd, while only Cr was preferentially retained over Pb. Soil type did not substantially influence breakthrough time for the acidic metals waste, particularly Cd (Table 5), indicating that the properties of this waste solution were more important for metal retention than the properties of the soil.

Cadmium and Pb mobilities were also enhanced in the synthetic landfill leachate. This was probably due to complexation of the metals by the organics in the solution. Knox and Jones (1979) reported that three sanitary landfill leachates tested were able to complex Cd to some extent, although their ability to do so varied, and in some cases might well have been insufficient to greatly affect metal removal from solution. It has been noted that mobility of Cd and Pb in soil was increased by complexation of Cd (Doner, 1978; Benjamin and Leckie, 1982; Garcia-

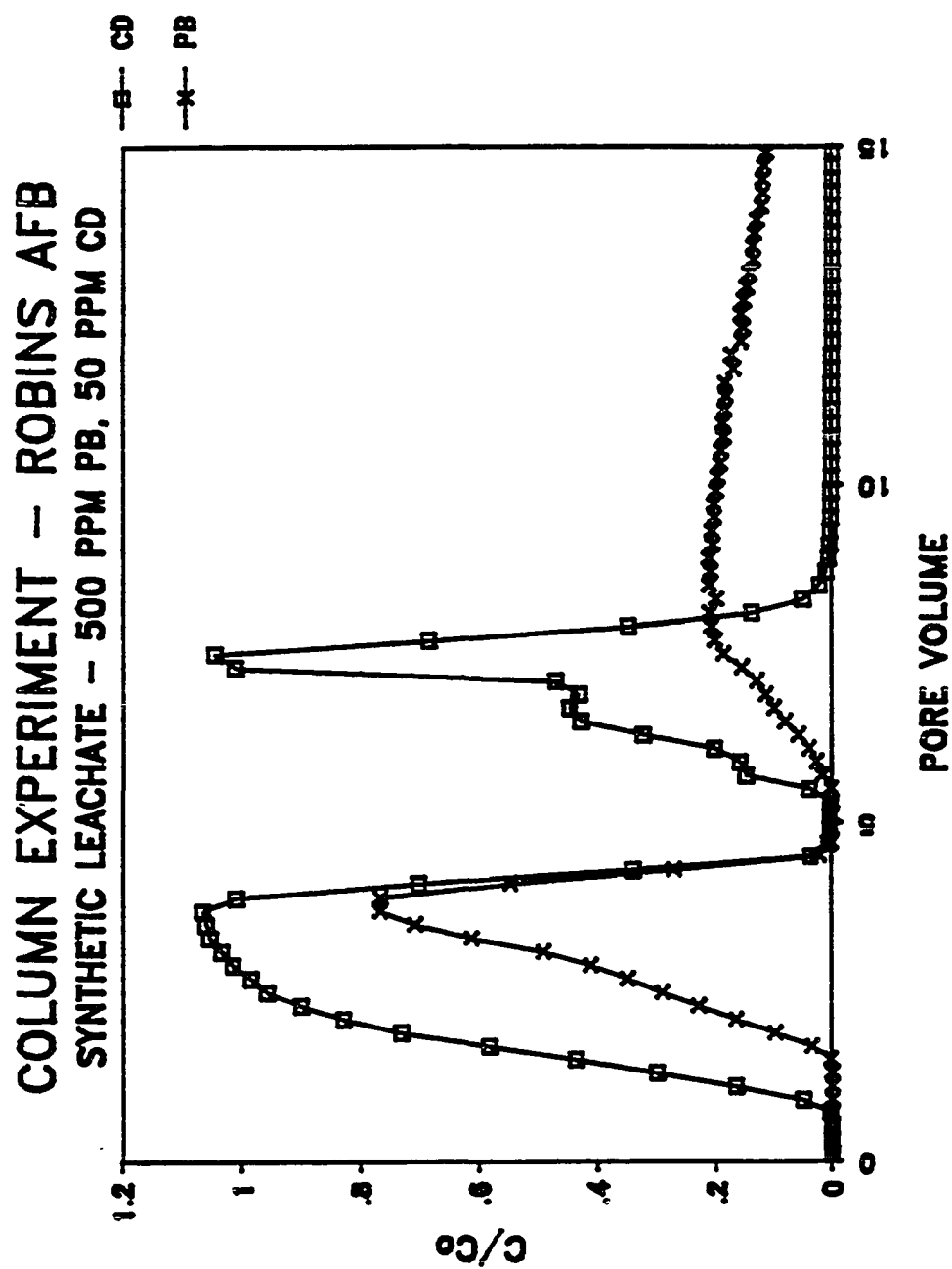


Figure 10. Breakthrough curves of all metals for the acidic metals waste containing $500 \text{ mg}\cdot\text{L}^{-1}$ Pb and $50 \text{ mg}\cdot\text{L}^{-1}$ Cd for the Norfolk subsoil.

Miragaya and Page, 1976; LaBauve et al., 1988) and Pb (Brown, 1979; LaBauve et al., 1988). Zinc migration through soil has been reported to be facilitated by higher total organic carbon and total soluble salts levels in a municipal solid waste leachate (Boyle and Fuller, 1987).

Two peaks were in evidence for Cd and Pb for the synthetic leachate solution applied to the Norfolk soil (Figure 11). This would indicate that there are at least two species of Pb and Cd present. The effluent for the first peak had a pink coloration, while the effluent for the second peak was colorless. Breakthrough for the first peak of Cd and Pb in the synthetic leachate occurred prior to breakthrough for Cd and Pb in $\text{Ca}(\text{NO}_3)_2$, while breakthrough of the second peak occurred later than any other peak (Table 5). The solution, prior to addition to the soil, was colorless, indicating that the formation of the complex required an interaction with the soil. The easily reducible Mn oxides may have reacted with organic ligands leading to polymerization of the organic ligands and resulting in colorization of the solution (McBride, 1987; Shindo and Huang, 1982, 1984; Stone and Morgan, 1984a,b).

Mobility of Cd and Pb in the simulated oil field waste was reduced compared to $\text{Ca}(\text{NO}_3)_2$, indicating that a mechanism for enhanced retention existed. It is possible that the Cr(III) in the oil field waste precipitated as the hydroxide, with the metals co-precipitating with the Cr(III). As pH increased above pH 4, precipitation of Cr(III) as an amorphous hydrated hydroxide can occur (Griffin and Shimp, 1978). Breakthrough of Cd and Ba was similar and occurred before Pb. Chromium(III) did not elute from the columns receiving the synthetic oil field waste (Figure 12). Griffin and Shimp (1978) stated that the relative mobility of heavy metals in clays, as determined from equilibrium

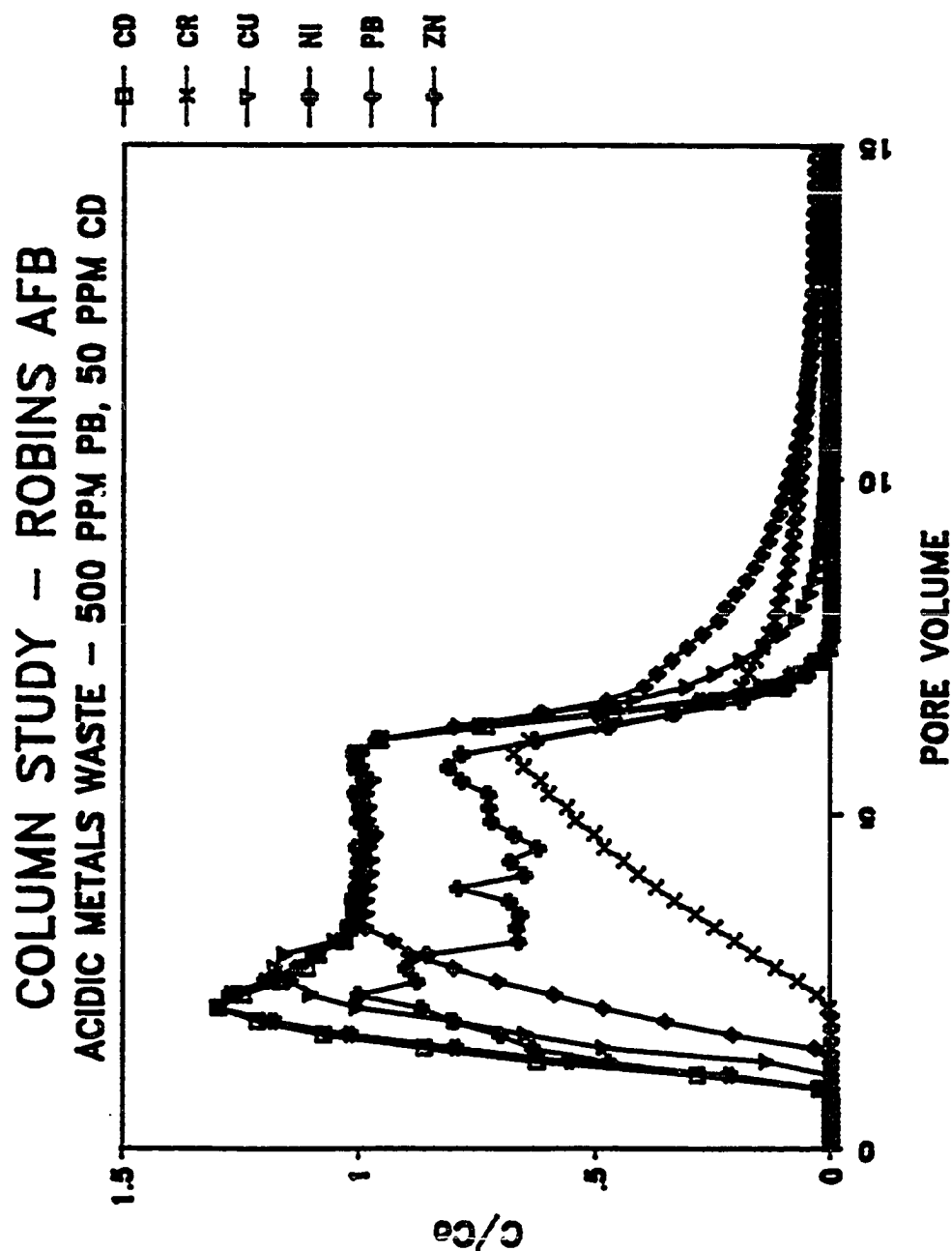


Figure 11. Breakthrough curves for Cd and Pb for the synthetic leachate solution containing $500 \text{ mg}\cdot\text{L}^{-1}$ Pb and $50 \text{ mg}\cdot\text{L}^{-1}$ Cd for the Norfolk subsoil.

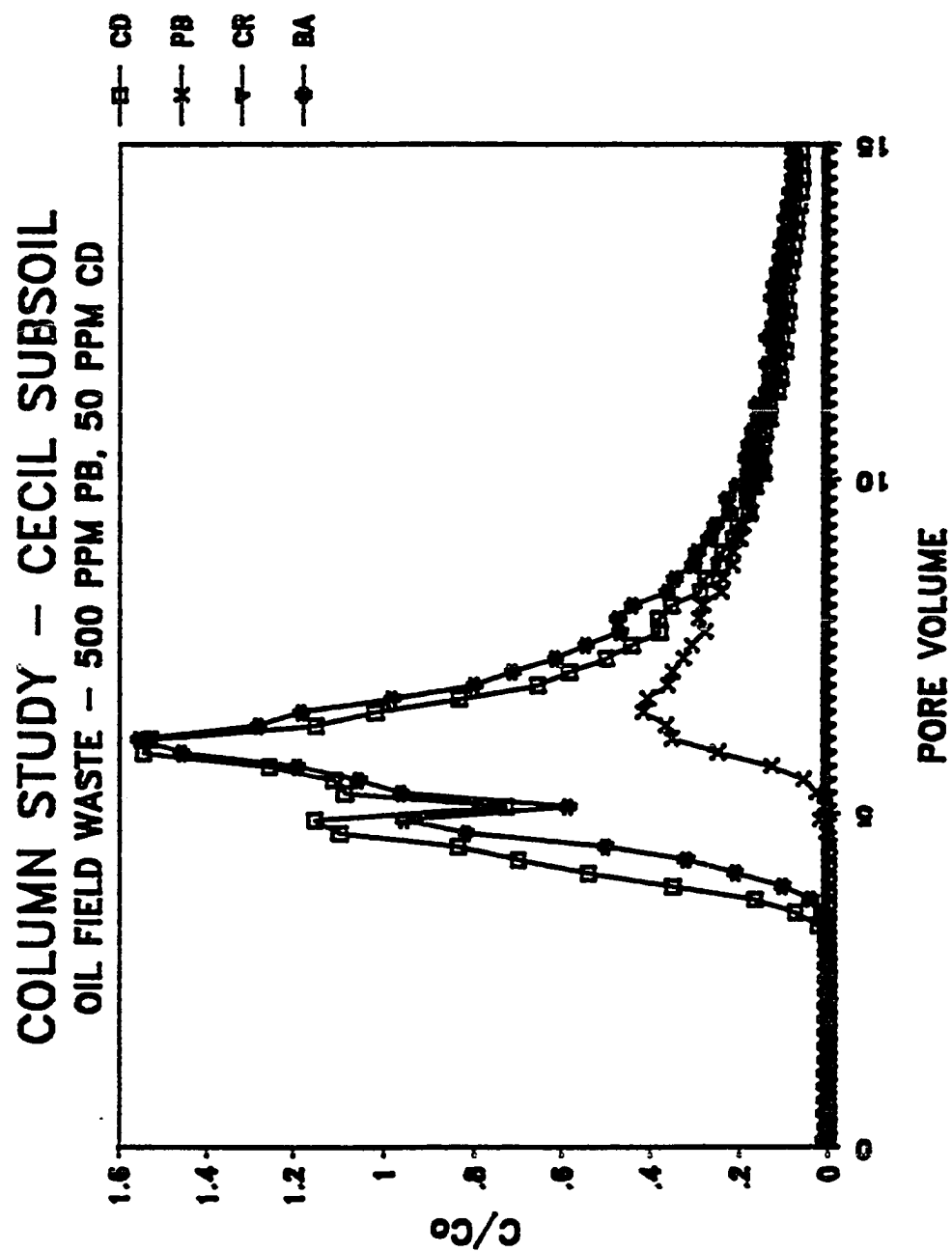


Figure 12. Breakthrough curves of all metals for the oil field waste solution containing $500 \text{ mg}\cdot\text{L}^{-1}$ Pb and $50 \text{ mg}\cdot\text{L}^{-1}$ Cd for the Cecil subsoil.

retention data from pure solutions of metals at pH 5, were: $\text{Cd} > \text{Pb} > \text{Cr(III)}$, which is in agreement with the results of Fuller (1980) and of this study.

Recovery was typically less than 100% for Pb in both soils (0-100%) and for Cd in the Cecil soil (25-100%), except for the acidic metals waste where recovery was typically greater than 90% (Table 5). No Cd was retained by the Norfolk soil after leaching with 15 PV of 0.005M $\text{Ca(NO}_3)_2$ for any solution. Recovery of Pb was typically greater for the Norfolk than for the Cecil soil. Greater recoveries for the metals would have occurred if leaching was extended beyond 15 PV, as evidenced by the tailing.

It should be noted that breakthrough of Cd in the acidic metals waste for both soils occurred at less than 1.5 pore volumes. A breakthrough at 1 pore volume indicates no reaction between the solute and the soil. Therefore, Cd in the acidic metals waste reacted very little with the soil which is likely a result of the high H^+ activity more effectively competing for sorption sites and minimal metal precipitation reactions.

Reduced concentration (C/C_0) values in some cases exceeded one for acidic metals waste (Figures 3, 5, 6, 7), oil field waste (Figures 3, 6, 7), and $\text{Ca(NO}_3)_2$ (Figure 7). This was probably due to the chromatographic effect (Valocchi et al., 1981) which causes the concentration of a sorbing component to rise above its source strength. A second, more retarded component (another chemical species or element) moves through the soil and displaces the mass of the first component off the surface and into the aqueous phase (Reeves and Kirkner, 1988). For example, for the acidic metals waste (Figure 10), C/C_0 exceeded one for Cd, Zn, and Cu. Lead and

Cr, the more retarded components, may have displaced Cd, Zn, and Cu from the surface and into the aqueous phase, causing the concentrations of Cd, Zn, and Cu to rise above their source strength. For the oil field waste, Cd and Ba were displaced by the more retarded components of the solution, Pb and Cr, causing C/Co to exceed one for Cd and Ba (Figure 12).

Reaction of the solute with the soil will retard the movement of the solute through the soil. These reactions include adsorption and/or precipitation-type reactions. The trace and toxic metals are typically retained more strongly by the soil than are the major cations (Ca, Mg, Na, K). The stronger the retention mechanism, the longer it will take for the metal to move through the soil column. Thus Cr was held the most tightly by the soil. Also the Cecil subsoil, with its greater oxides and clay contents, was able to bind the metals more strongly by adsorption and/or precipitation-type reactions.

The distribution ratio (K_D), the ratio of concentration of metal sorbed to the concentration in solution, was determined in the batch (Freundlich) study (Chapter 5) and this column transport study. The results did not always agree between the two methods (Table 6). For Pb, the batch K_D was greater than the column K_D in the Cecil subsoil. For Cd, the batch K_D was less than the column K_D in the Robins (Norfolk) subsoil. Therefore, batch K_D 's may not always predict column K_D values.

Reasons for the lack of agreement between batch and column K_D values in some cases are not well understood and are the subject of much debate between investigators (Miller et al., 1989). It should be realized that a multiplicity of reactions covering a continuum of reaction rates probably occurs from the beginning of contact between solute and soil. Although the column residence times (see Chapter 7) were sufficient for

Table 6. Comparison of K_D values by column and batch methods.

Soil, Solution, and Metal Concentration	K_D (Column)		K_D (Batch)	
	Cd	Pb	Cd	Pb
Cecil				
Ca(NO ₃) ₂ - 50 Pb/5 Cd	2.05	-	1.59	14.08
- 500 Pb/50 Cd	0.91	1.48		
Syn Leach - 50 Pb/5 Cd	0.92	1.25	0.31	4.56
- 500 Pb/50 Cd	0.37	0.81		
Acidic Metals - 50 Pb/5 Cd	0.04	0.59	0.08	1.30
- 500 Pb/50 Cd	0.15	0.51		
Oil Field - 50 Pb/5 Cd	1.83	-	1.88	50.52
- 500 Pb/50 Cd	1.20	1.37		
Norfolk				
Ca(NO ₃) ₂ - 50 Pb/5 Cd	1.81	-	0.16	2.29
- 500 Pb/50 Cd	0.566	1.70		
Syn Leach - 50 Pb/5 Cd	0.61/3.52	-	0.07	0.64
- 500 Pb/50 Cd	0.36/3.76	1.09/3.52		
Acidic Metals - 50 Pb/5 Cd	0.24	1.50	0.09	0.18
- 500 Pb/50 Cd	0.24	0.72		
Oil Field - 50 Pb/5 Cd	2.58	5.54	0.09	2.19
- 500 Pb/50 Cd	1.11	2.0		

the more rapid surface reactions to attain equilibrium, the local equilibrium assumption was probably not applicable to all reactions that were occurring. Slowly reversible and irreversible reactions (by definition) would not attain equilibrium in the time periods used. Similar arguments hold for the batch experiment even with a longer reaction time (24 hr for the batch versus the shorter column residence times). Since the distribution of solute between soil and solution is a result of all reactions occurring, different time frames between the column and batch experiments may explain part of the differences observed. Also, the column K_D assumed the Freundlich parameter to be unity, which was not always true, as seen in the batch experiment (Chapter 5). Good agreement between batch and column K_D values was observed in some cases, and, in those systems, the more rapid surface reactions apparently control solute distribution between soil and solution. Agreement or lack of agreement depends on the element, soil, and composition of the waste solution, thus more complex factors than time are involved.

SUMMARY AND CONCLUSIONS

The sandy Norfolk soil had a low retention capacity, and thus breakthrough occurred early in this soil. Breakthrough of Cd occurred prior to Pb for both soils and all solutions. Breakthrough of higher concentrations of Cd and Pb was faster than at lower concentrations for all solutions. For the different waste solutions, breakthrough occurred in the order: acidic metals waste > synthetic leachate > 0.005M $\text{Ca}(\text{NO}_3)_2$ > oil field waste. Competition between different metals and low pH of the acidic metals waste solution prevented retention of Cd and Pb by the

soils. There appeared to be at least two species of Pb and Cd in the synthetic leachate during transport through the Norfolk soil. It appeared that Cd and Pb were co-precipitated with Cr(III), increasing their retention compared to the $\text{Ca}(\text{NO}_3)_2$.

Waste solutions can greatly affect metal retention by soils. The composition of the waste solution may override soil factors in controlling trace metal mobility. In this study, the composition of the acidic metals waste was more important than the soil factors in dictating Cd and Pb transport through the soil.

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CHAPTER 8

SUMMARY AND CONCLUSIONS

The transport of metals to groundwater below hazardous waste sites is of great environmental concern. The movement of a particular metal is determined by (1) the soil's chemical and physical properties, (2) the amount and form of the metal, and (3) the composition of the soil or waste solution with which the metal is associated. The soil properties controlling Pb retention and mobility were pH, CEC, metal oxides (Mn oxides, amorphous Fe oxides, and free Fe oxides), and particle-size distribution. For Cd, pH, CEC, amorphous Fe oxides, and particle-size distribution controlled retention. Copper mobility was controlled by the three metal oxides. The Fe oxides (amorphous and crystalline) controlled Ni and Zn retention. Arsenic retention was controlled by pH, CEC, and the metal oxides. Redox potential also influenced Cd and Pb retention, with greater metal retention under oxidizing conditions.

The greater the concentration of Cd and Pb added to the soil, the lower the proportion of the metal retained. Therefore, the greater the concentration of the metal, the faster it will move through the soil. The retention of Pb was greater than Cd.

The retention of Cd and Pb were affected by solution composition. Retention of the metals was greater in a dilute salt solution (0.005M $\text{Ca}(\text{NO}_3)_2$) and in a simulated oil field waste and was less in a synthetic

municipal landfill leachate and simulated acidic metals waste. Organic complexation of Cd and Pb reduced their retention, and thus increased their mobility. The low pH of the acidic metals waste and competition from other metals reduced Cd and Pb retention in this waste. Therefore, it can be concluded that the composition of the waste solution may override soil factors in controlling trace metal mobility.

Comparing the field studies of sites with metal contamination with laboratory studies with uncontaminated soils and simulated wastes, it can be concluded that laboratory batch studies can be used to qualitatively predict trace metal mobility in soils. However, site specific conditions do not permit quantitative predictions from batch results.

VITA

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She graduated from Rahway High School, Rahway, New Jersey, in June 1978 and entered Muhlenberg College in August 1978. She graduated in May 1982 with a B.S. in Chemistry and Natural Sciences and Mathematics.

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